Supporting Information

Direct Access to 2-Amino-3-cyano-4H-pyrans/ 4H-chromenes by [ONO]-Pincer Supported Nickel(II) Phosphine Complexes via Dehydrogenative Annulation of Alcohols

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1. Materials and methods

Chemically pure and analar grade reagents were used for all the reactions. Commercially available [$NiCl_2(PPh_3)_2$], N-diethyamino benzaldehyde derivatives, hydrazide derivatives, dimedone, 4-hydroxycoumarin, $CDCl_3$, DMSO-d_6 and various alcohols was used as supplied from Sigma Aldrich. The solvents were freshly distilled before use following the standard procedures.[1] Melting point was recorded in the Boeties micro heating table and is uncorrected. Infrared spectra of complexes were recorded in KBr pellets with a Perkin – Elmer 597 spectrophotometer in the range of 4000-400 cm^{-1}. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 with Bruker 400 MHz instrument using TMS as internal reference. High-Resolution mass spectrometry are recorded with Agilent QTOF G6545XT spectrometer at 50000 resolution using ESI mode.

2. X-ray crystallographic data collection

A single crystal with high quality and exhibiting good morphology was chosen for X-ray diffraction intensity measurements. The X-ray diffraction intensity data was collected at room temperature (293 K) on a Bruker D8 Quest Eco diffractometer using MoKα radiation (0.71073 A°). During the data collection, the crystal to detector distance was set to 4.5 cm. The data collection was monitored by APEX-III program suit.[2] further, the integration, Lorentz and polarization corrections and merging of data were carried out using SAINT. The absorption correction was performed by SADABS and the data was averaged using SORTAV software.[3] The hydrogen atoms of all C−H, N−H and O−H hydrogen bonds were located from the difference Fourier map and were refined isotropically. Idealized methyl group H-atom position was calculated geometrically [C−H = 0.96 A]° and refined using riding model with Uiso(H) = 1.5 Ueq (C). The structure was solved by direct methods using SHELXS-2014[4] and refined by SHELXL-2014 [5] programs incorporated to WINGX package.[6] The ORTEP of the molecule with displacement ellipsoids drawn at 30% probability level are shown in **Figure 2**. The molecular and packing diagrams were generated using the software MERCURY.[7]

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Table S1. Crystal data and structure refinement for complex C2.

CCDC	2334596
Empirical formula	$C_{34}H_{32}N_3NiO_3P$
Formula weight	620.30
Temperature/K	295(2)
Crystal system	triclinic
Space group	P-1
a/Å, b/Å, c/Å	11.9646(10), 16.0861(12), 16.6355(15)
α/°, β/°, γ/°	74.568(7), 78.164(8), 79.707(7)
Volume/Å^3	2994.4(5)
Z	4
ρcalc g/cm3	1.376
μ /mm-1	0.741
F(000)	1296.0
Crystal size/mm	0.35 × 0.17 × 0.12
2Θ for data collection/°	6.7 to 62.888
Index ranges	$-14 \le h \le 16$, $-22 \le k \le 21$, $-22 \le l \le 22$
Reflections collected	30127
Independent reflections	14124 [R_{int} = 0.1420, R_{sigma} = 0.1957]
Data/restraints/parameters	14124/0/761
Goodness-of-fit on F^2	1.151
Final R indexes [I>2σ (I)]	R_1 = 0.1453, wR_2 = 0.3398
Final R indexes [all data]	R_1 = 0.2361, wR_2 = 0.4120
Largest diff. peak and hole / eÅ^{-3}	4.23/-1.01

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Table S2. Selected bond lengths (Å) and bond angles (°) for complexes C2.

	Complex C2
Ni1–P1	2.2073(19)
Ni1–O1	1.817(5)
Ni1–N1	1.839(6)
Ni1–O2	1.803(5)
O1-Ni1-P1	90.48(18)
O1-Ni1-N1	84.3(3)
N1-Ni1-P1	174.8(2)
O2-Ni1-P1	89.51(15)
O2-Ni1-O1	177.4(2)
O2-Ni1-N1	95.7(2)

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3. IR Spectra of the complexes C1-C3:

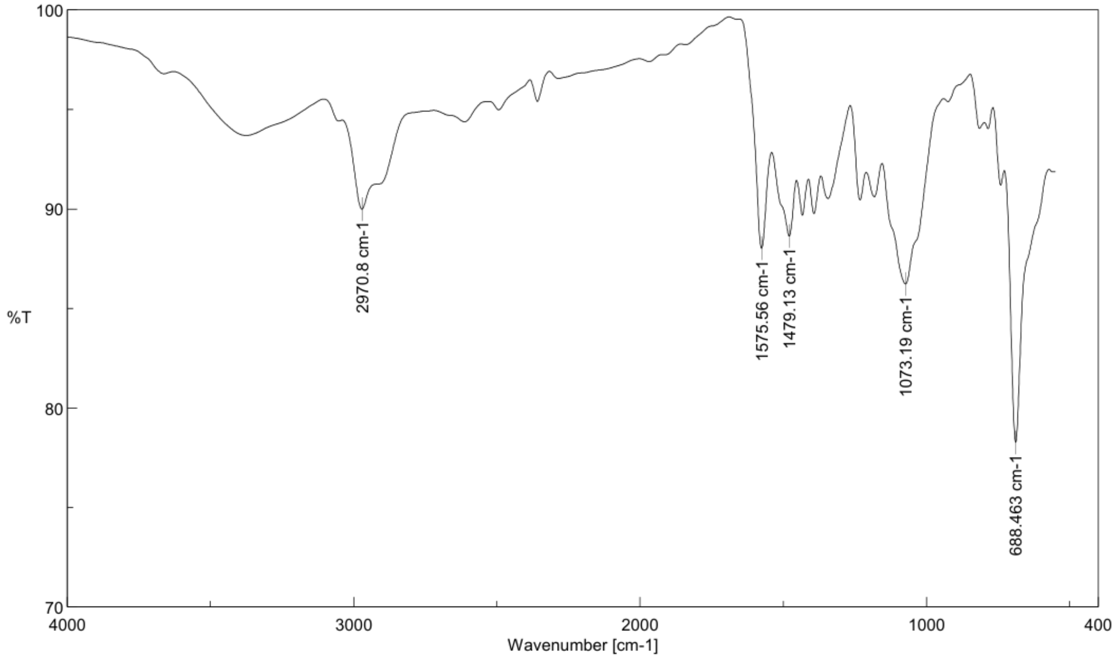

Figure S1. FT-IR spectrum of Complex **C1**

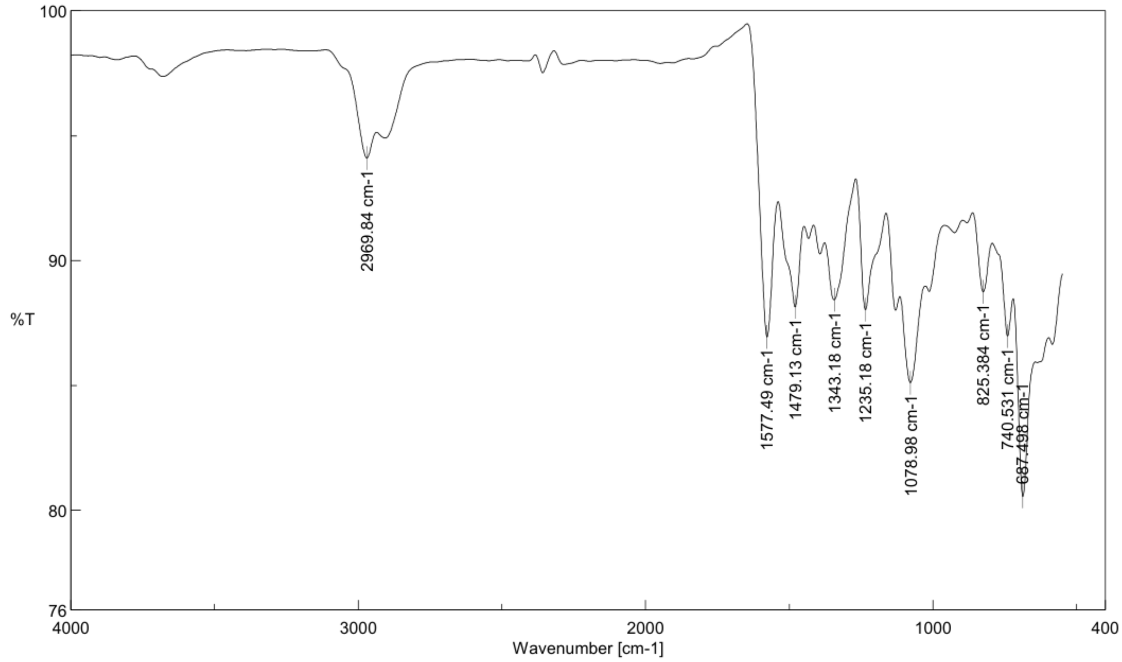

Figure S2. FT-IR spectrum of Complex **C2**

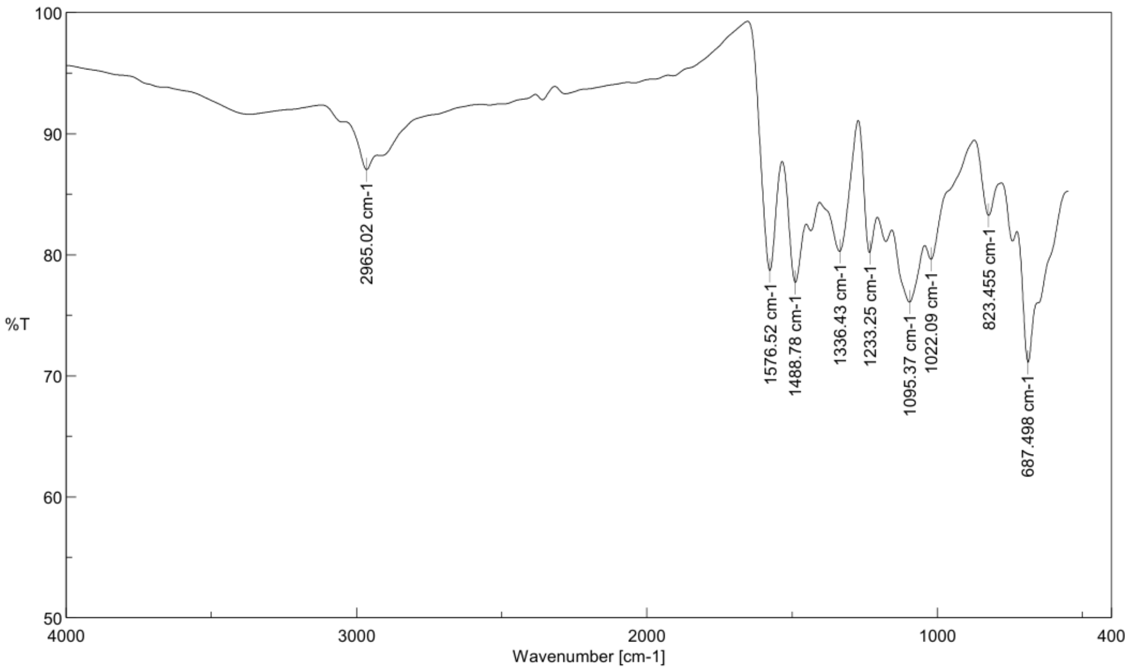

Figure S3. FT-IR spectrum of Complex **C3**

4. NMR spectra of Ni(II) NNO complexes C1-C3

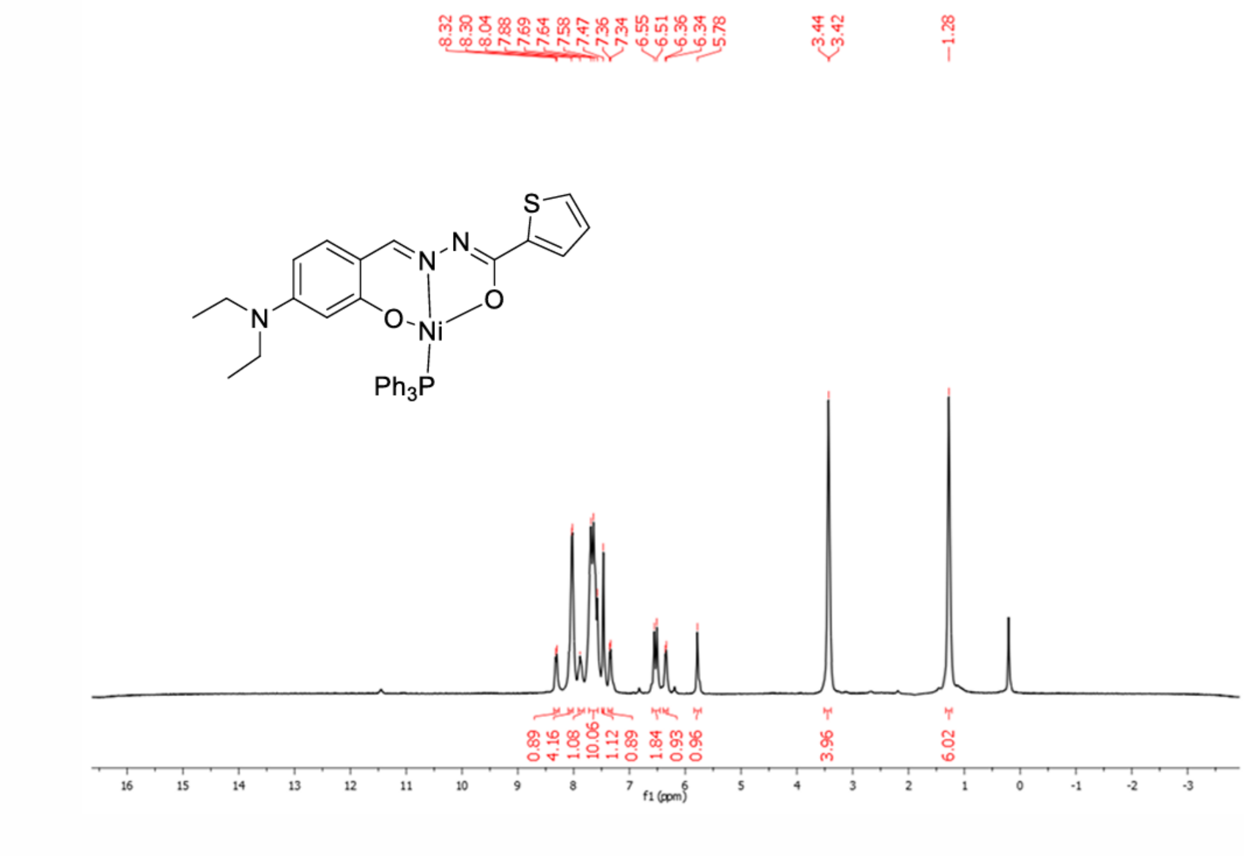

Figure S4. [1]H NMR spectrum of complex **C1** in $CDCl_3$ (400 MHz, 293 K).

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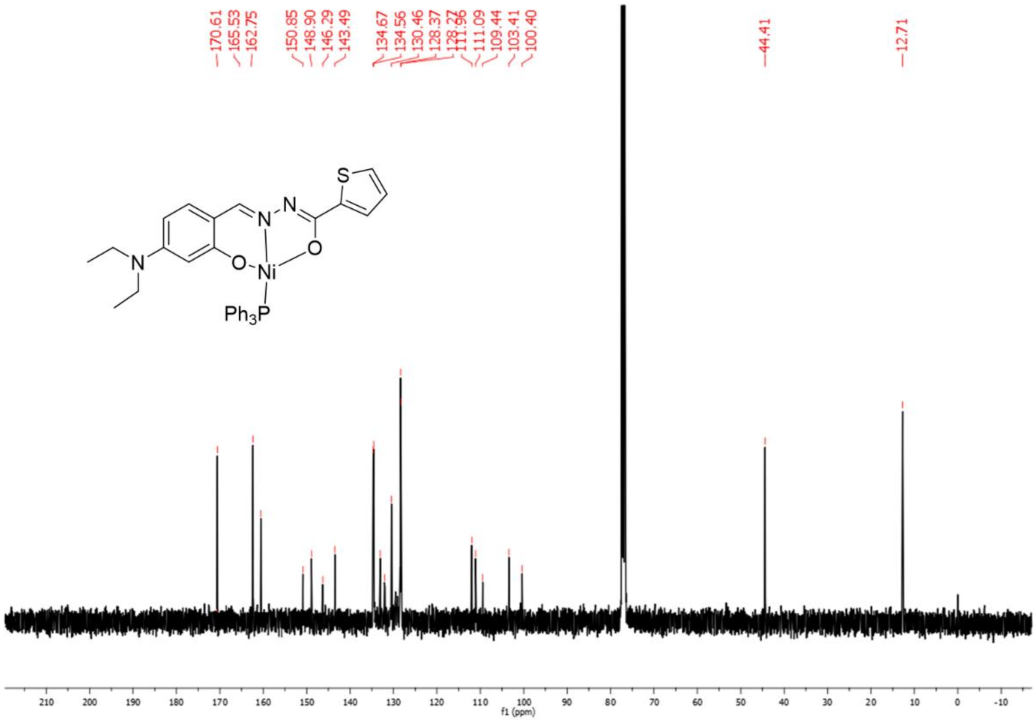

Figure S5. $^{13}C\{^1H\}$ NMR spectrum of complex **C1** in $CDCl_3$ (100 MHz, 293 K).

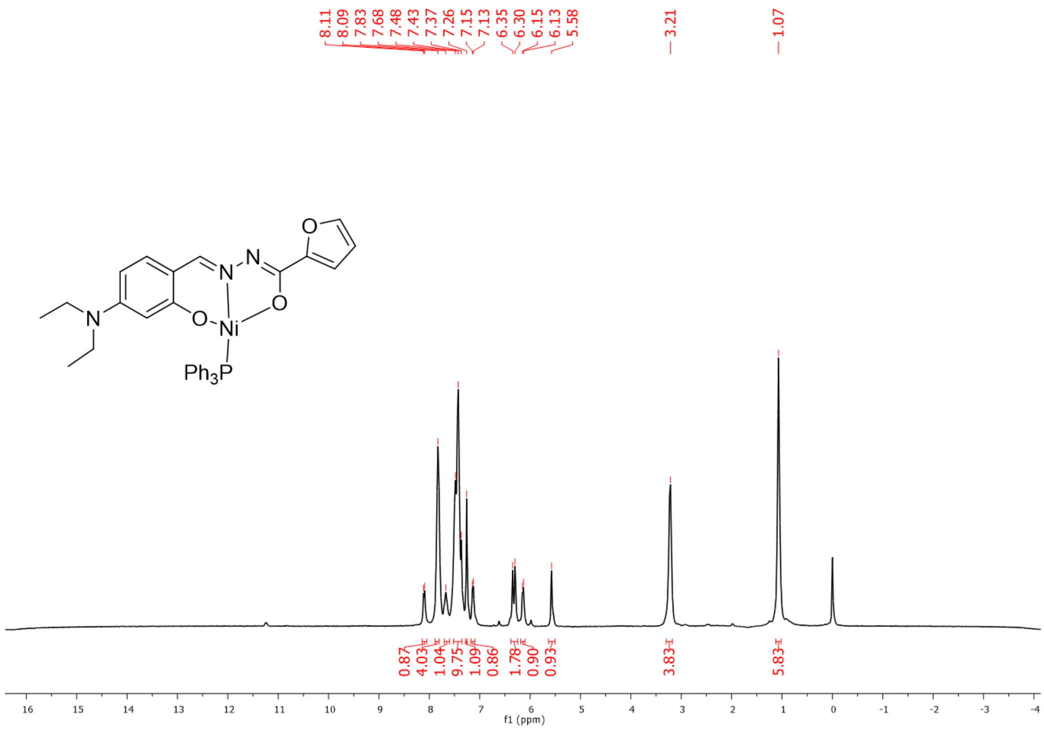

Figure S6. ^1H NMR spectrum of complex **C2** in $CDCl_3$ (400 MHz, 293 K).

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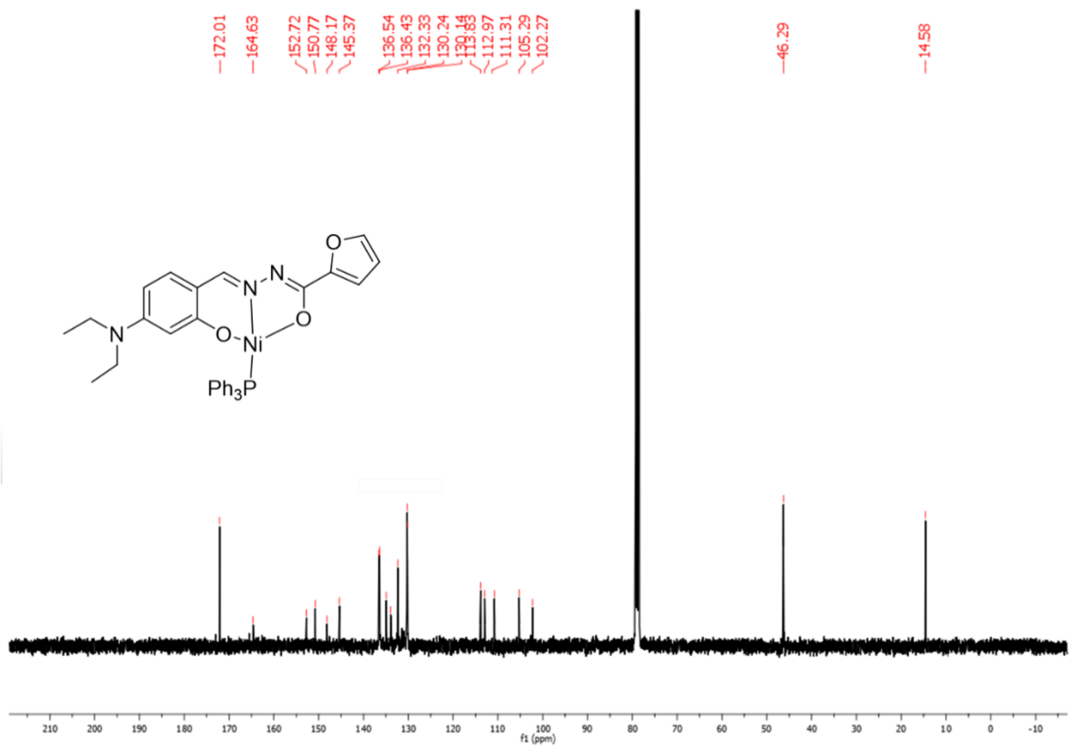

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of complex **C2** in $CDCl_3$ (100 MHz, 293 K).

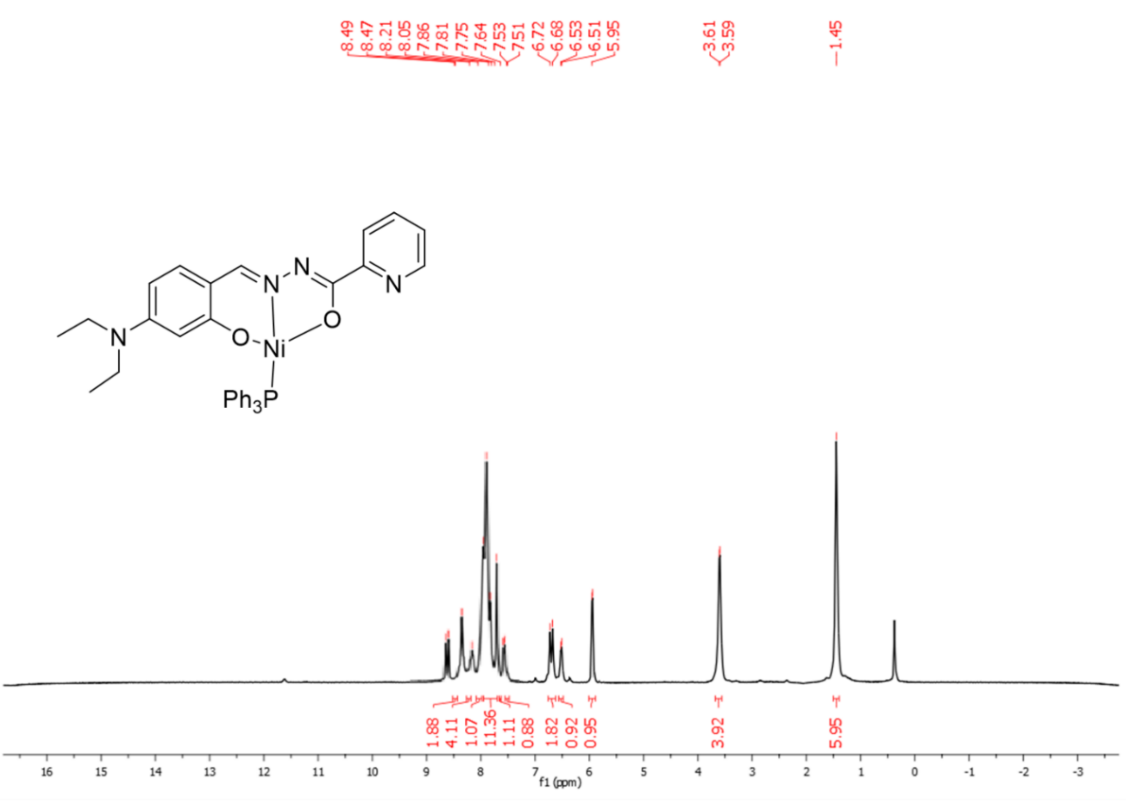

Figure S8. ^{1}H NMR spectrum of complex **C3** in $CDCl_3$ (400 MHz, 293 K).

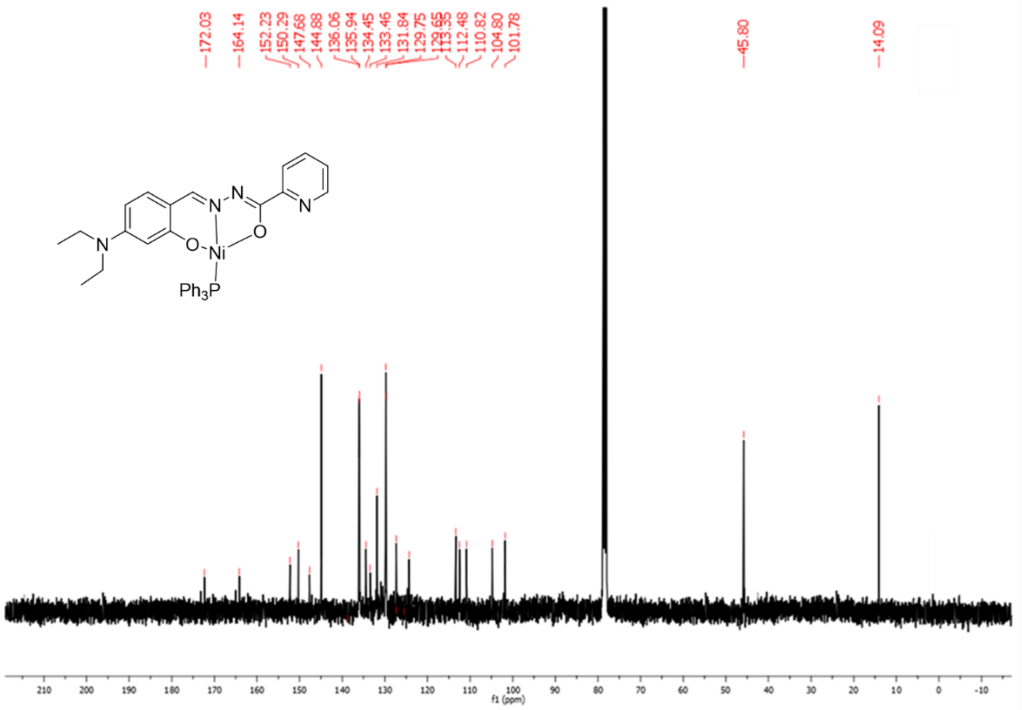

Figure S9. $^{13}C\{H\}$ NMR spectrum of complex **C3** in $CDCl_3$ (100 MHz, 293 K).

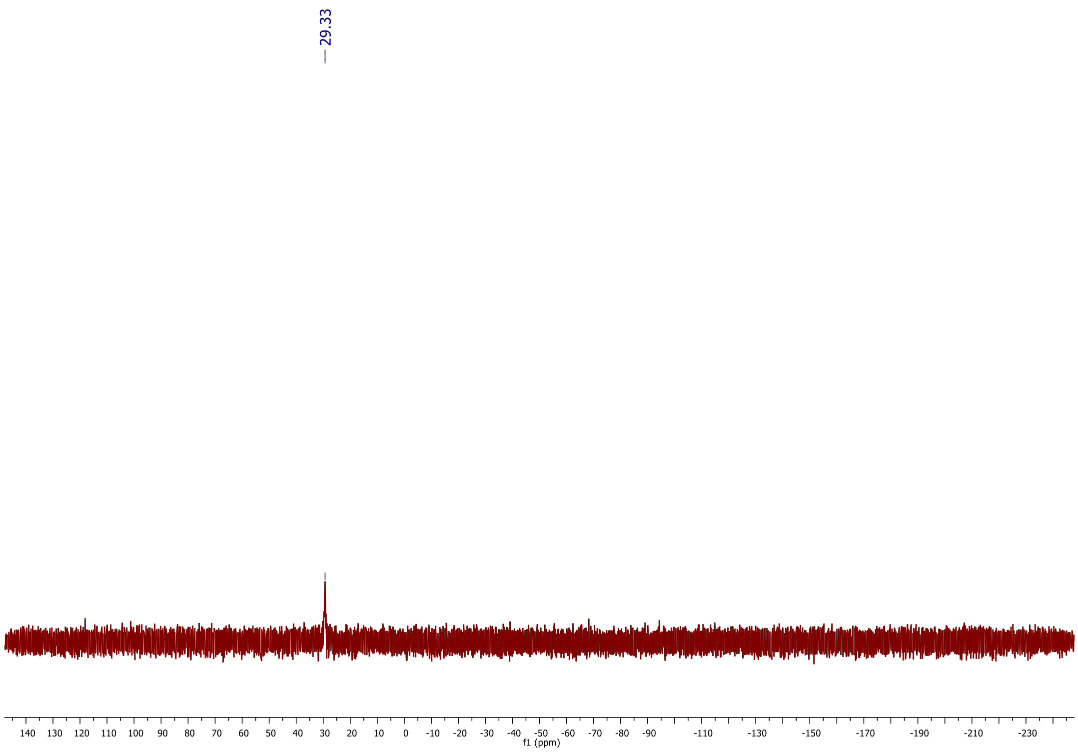

Figure S10. $^{31}P\{^1H\}$ NMR spectrum of complex **C1** in $CDCl_3$ (162 MHz, 293 K).

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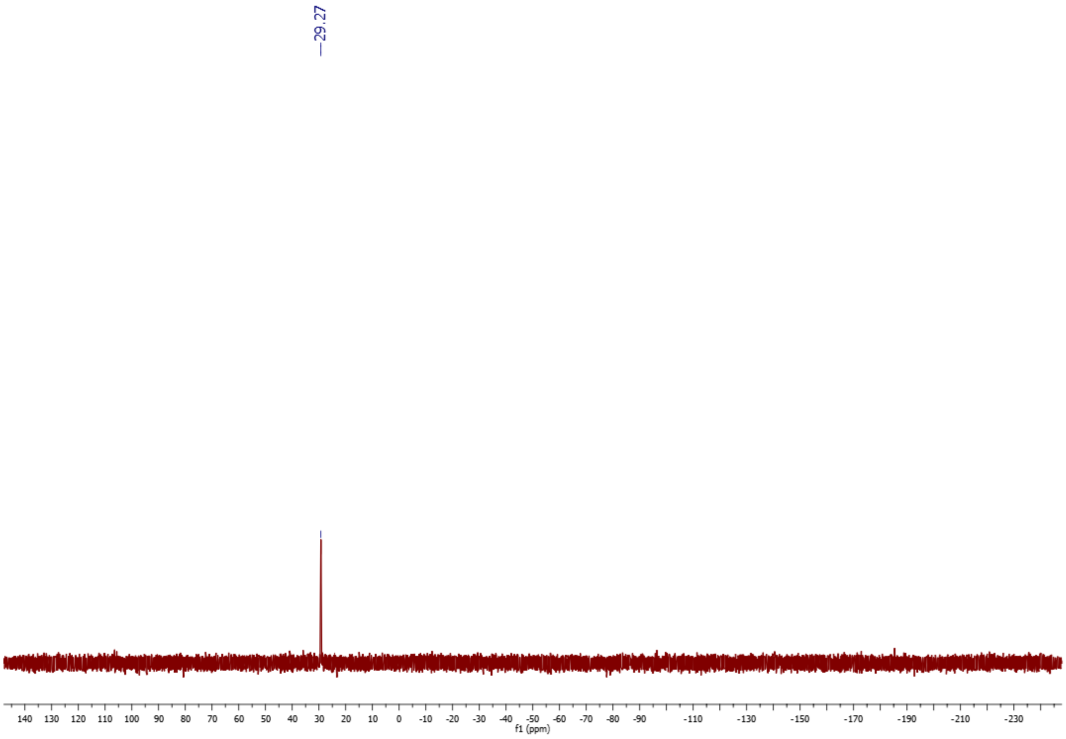

Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of complex **C2** in $CDCl_3$ (162 MHz, 293 K).

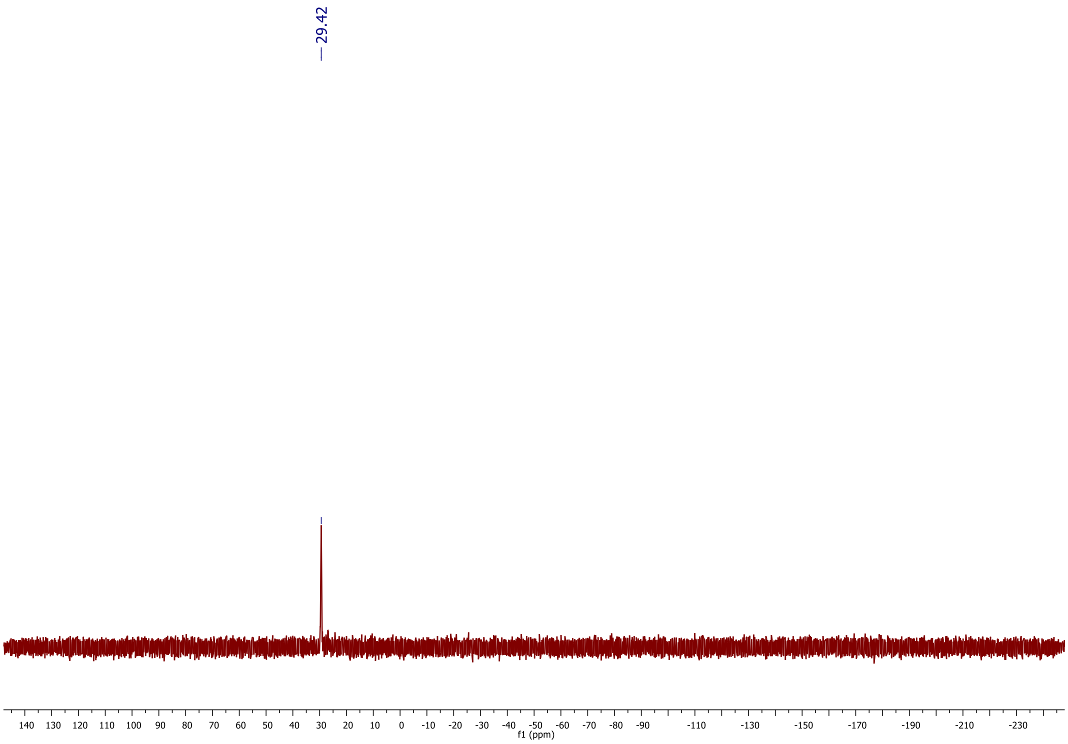

Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of complex **C3** in $CDCl_3$ (162 MHz, 293 K).

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5. HRMS spectra of Ni(II) complexes C1-C3

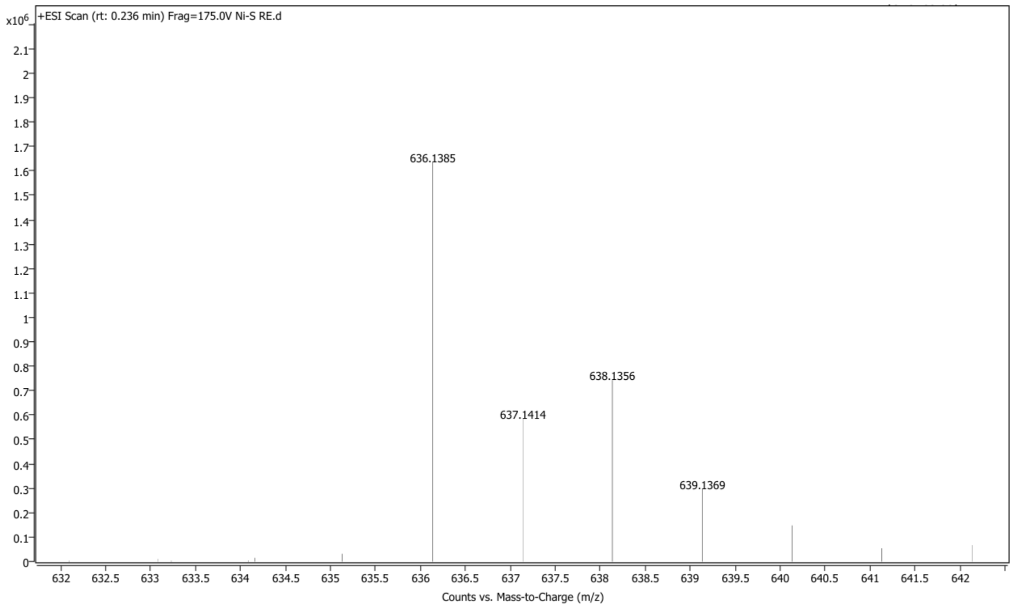

Figure S13. HRMS spectrum of complex **C1,** Calculated: 636.1385 $[M]^+$; Found: 636.1385 $[M]^+$.

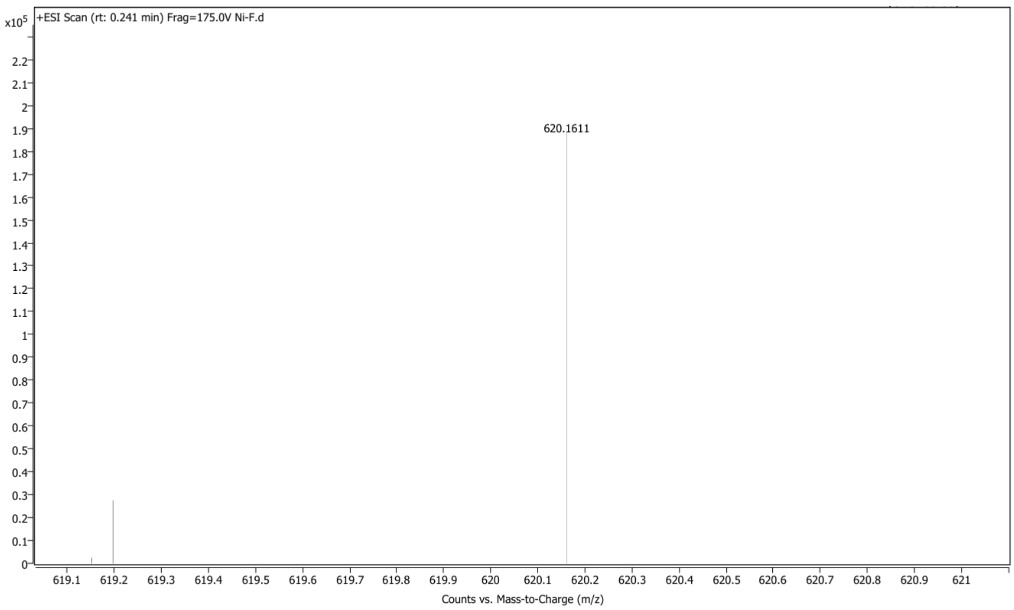

Figure S14. HRMS spectrum of complex **C2,** Calculated: 620.1613 $[M]^+$; Found: 620.1611 $[M]^+$

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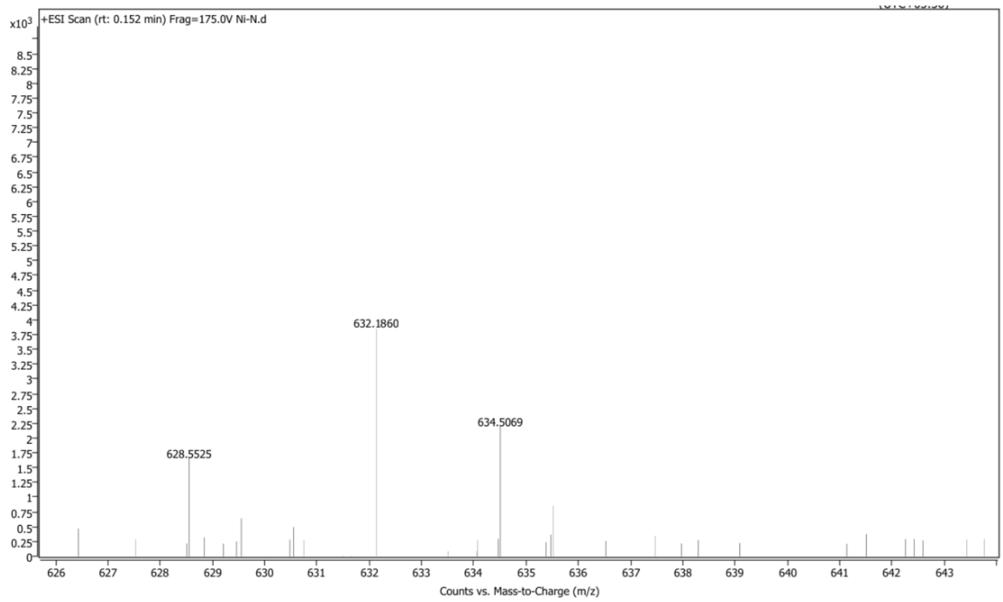

Figure S15. HRMS spectrum of complex **C3,** Calculated: 632.1851 $[M+H]^+$; Found: 632.1860 $[M+H]^+$

6. Characterisation data of products:

2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4a)***[8]:
white solid (yield: 257 mg, 91%). ^{1}H NMR (400 MHz, DMSO) δ 7.28 (t, 2H), 7.19 – 7.13 (m, 3H), 6.99 (s, 2H), 4.17 (s, 1H), 2.51 (s, 2H), 2.25 (d, J = 7.2 Hz, 1H), 2.10 (d, J = 7.2 Hz, 1H), 1.00 (d, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 195.5, 162.4, 158.4, 144.7, 128.2, 127.1,126.5, 119.6, 112.7, 58.2, 49.9, 35.5, 31.7, 28.3, 26.7.

2-amino-7,7-dimethyl-5-oxo-4-(p-tolyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4b)***[8]:
white solid (yield: 277 mg, 62%). ^{1}H NMR (400 MHz, DMSO) δ 7.01 (t, 2H), 6.87 (d, J = 7.2 Hz, 2H), 6.72 (s, 2H), 3.90 (s, 1H), 3.09 (s, 3H), 2.24 (s, 2H), 1.98 (d, J = 7.2 Hz, 1H), 1.83 (d, J = 7.2 Hz, 1H), 0.75 (d, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 196.1, 164.0, 159.1, 144.0, 132.3, 131.7, 131.4, 130.0, 128.6, 119.5, 111.4, 32.2, 28.7, 27.3.

2-amino-7,7-dimethyl-5-oxo-4-(m-tolyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4c)***[9]:
white solid (yield:255 mg, 83%). ^{1}H NMR (400 MHz, DMSO) δ 7.29 (d, J = 7.2 Hz, 2H), 7.16 (d, J = 7.2 Hz, 2H), 7.01 (s, 2H), 4.19 (s, 1H), 2.52 (s, 2H), 2.28 (s, 2H), 1.61 (s, 3H), 1.01 (d, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 195.3, 165.2, 158.2, 144.4, 128.0, 126.9, 119.4, 112.5, 58.0, 49.7, 47.4, 35.3, 31.5, 28.1, 26.5.

2-amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4d)***[8]:
white solid (yield:288 mg, 89%). ^{1}H NMR (400 MHz, DMSO) δ 7.05 (d, J = 7.2 Hz, 2H), 6.92 (d, J = 7.2 Hz, 2H), 6.77 (s, 2H), 3.95 (s, 1H), 3.31 (s, 3H), 2.28 (s, 2H), 1.90 (s, 2H), 0.77 (d, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 196.1, 162.8, 158.9, 141.9, 136.5, 128.3, 126.4, 120.1, 113.0, 58.6, 50.4, 35.57, 32.2, 28.8, 27.2, 15.1.

2-amino-4-(2,3-dimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4e)***[9]:
white solid (yield:286 mg, 81%). ^{1}H NMR (400 MHz, DMSO) δ 7.03 (d, J = 7.2 Hz, 1H), 6.90 (d, J = 7.2 Hz, 2H), 6.75 (s, 2H), 4.07 (s, 1H), 3.49 (s, 3H), 3.29 (s, 2H), 2.27 (s, 2H), 1.88 (s, 2H), 0.75 (d, J = 7.2 Hz,

6H). ^{13}C NMR (100 MHz, DMSO) δ 196.3, 163.2, 159.2, 145.4, 129.0, 127.9, 127.3, 120.4, 113.5, 59.0, 55.5, 50.7, 46.3, 36.3, 32.5, 29.1, 27.5.

2-amino-7,7-dimethyl-5-oxo-4-(2,3,4-trimethoxyphenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4f)***:
white solid (yield:303 mg, 79%). ^{1}H NMR (400 MHz, DMSO) δ 6.45 (s, 2H), 4.76 (s, 2H), 4.35 (s, 1H), 3.83 (d, J = 7.2 Hz, 9H), 2.48 (s, 2H), 2.27 (s, 2H), 1.12 (d, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 196.0, 161.8, 157.6, 153.2, 139.0, 136.9, 118.8, 113.8, 104.6, 63.0, 60.7, 56.1, 50.6, 40.7, 35.7, 32.1, 29.1, 27.3. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{24}N_2O_5$: 385.1763; observed: 385.1763.

2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4g)***[8]:
white solid (yield:276 mg, 84%). ^{1}H NMR (400 MHz, DMSO) δ 7.16 – 7.12 (m, 2H), 7.03 (t, 2H), 6.88 (s, 2H), 4.14 (s, 1H), 2.45 (s, 2H), 2.19 (d, J = 7.2 Hz, 1H), 2.05 (d, J = 7.2 Hz, 1H), 1.86 (s, 1H) 0.92 (d, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 196.4, 162.8, 162.0, 159.6, 158.4, 140.6, 128.9, 128.8, 119.6, 115.0, 114.8, 112.4, 111.7, 58.2, 49.8, 34.7, 31.6, 28.1, 26.6.

2-amino-4-(3-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4h)***[9]:
white solid (yield:233 mg, 71%). ^{1}H NMR (400 MHz, DMSO) δ 7.16 (t, 4H), 6.93 (d, J = 7.2 Hz, 2H), 5.39 (s, 1H), 23.6 – 2.25 (m, 4H), 1.08 (d, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 190.7, 189.4, 136.7, 131.5, 128.3, 128.2, 115.3, 47.0, 46.4, 32.4, 31.4, 29.7, 29.6, 27.4.

2-amino-4-(2,5-dichlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4i)***[9]:
white solid (yield:239 mg, 66%). ^{1}H NMR (400 MHz, DMSO) δ 7.30 (d, J = 7.2 Hz, 4H), 7.08 (d, J = 7.2 Hz, 2H), 5.54 (s, 1H), 2.76 (d, J = 7.2 Hz, 2H), 2.38 (d, J = 7.2 Hz, 2H), 1.22 (d, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 163.5, 158.6, 143.5, 131.8, 131.1, 130.8, 129.5, 128.1, 119.0, 110.9, 55.9, 4.8, 31.7, 28.2, 26.7.

2-amino-4-(4-cyanophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4j)***:
white solid (yield:204 mg, 64%). ^{1}H NMR (400 MHz, DMSO) δ 7.42 (d, J = 7.2 Hz, 1H), 7.30 (t, 1H), 7.22 (d, J = 7.2 Hz, 1H), 7.14 (s, 1H), 4.69 (s, 1H), 3.38 (s, 2H), 2.54 (s, 2H), 2.25 (d, J = 7.2 Hz, 1H), 2.11 (d, J = 7.2 Hz, 1H), 1.02 (d, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 165.6, 163.5, 158.6, 143.5, 131.8, 131.1, 130.8, 129.5, 128.1, 119.0, 110.9, 55.9, 49.8, 31.7, 28.2, 26.7. HRMS (ESI) m/z: $[M-H]^+$ calculated for $C_{19}H_{17}N_3O_2$: 318.1243; observed: 318.1249.

N-(4-(2-amino-3-cyano-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromen-4-yl)phenyl)acetamide ***(4k)***:
white solid (yield:256 mg, 73%). ^{1}H NMR (400 MHz, DMSO) δ 9.89 (s, 1H), 7.45 (d, J = 7.2 Hz, 2H), 7.05 (d, J = 7.2 Hz, 1H), 6.98 (s, 1H), 4.11 (s, 1H), 2.50 (d, J = 7.2 Hz, 3H), 2.26 – 2.07 (m, 2H), 2.01 (s, 3H), 0.99 (d, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 195.6, 168.0, 162.2, 158.3, 139.3, 137.7, 127.3, 119.7, 119.0, 112.7, 58.2, 49.9, 34.9, 31.7, 28.3, 26.7, 23.8. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{20}H_{21}N_3O_3$: 352.4138; observed: 352.4136.

4-([1,1'-biphenyl]-4-yl)-2-amino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4l)***:
white solid (yield:240 mg, 65%). ^{1}H NMR (400 MHz, DMSO) δ 8.41 (d, J = 7.2 Hz, 1H), 7.93 (d, J = 7.2 Hz, 1H), 7.79 (d, J = 7.2 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.53 – 7.45 (m, 1H), 7.28 (d, J = 7.2 Hz, 1H), 7.02, (s, 2H), 5.20 (s, 1H), 2.55 (d, J = 7.2 Hz, 2H), 2.26, (d, J = 7.2 Hz, 1H), 2.09 (d, J = 7.2 Hz, 1H), 1.03 (d, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 195.7, 195.7, 162.7, 158.4, 133.3, 130.7, 128.3, 126.9, 125.8, 125.6, 125.2, 123.6, 119.6, 119.6, 113.4, 58.9, 58.8, 50.0, 31.7, 28.3, 26.9. HRMS (ESI) m/z: $[M]^+$ calculated for $C_{24}H_{22}N_2O_2$: 370.1681; observed: 370.1680.

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2-amino-5-oxo-4-phenyl-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile ***(5a)***[8]:
white solid (yield:268 mg, 85%). ^{1}H NMR (400 MHz, DMSO) δ 8.45 (s, 1H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 3H), 7.06 (d, *J* = 7.2 Hz, 3H), 4.41 (s, 1H). ^{13}C NMR (100 MHz, DMSO) δ 164.7, 159.5, 157.9, 153.3, 152.0, 143.2, 128.4, 127.9, 12.5, 126.6, 123.8, 122.4, 103.9, 57.9.

2-amino-5-oxo-4-(p-tolyl)-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile ***(5b)***[8]:
white solid (yield:277 mg, 84%). ^{1}H NMR (400 MHz, DMSO) δ 8.41 (s, 1H), 7.88 – 7.82 (m, 2H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 3H), 7.10 (s, 1H), 7.00 (s, 2H), 4.37 (s, 1H), 2.23 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 165.7, 164.8, 161.2, 152.1, 145.6, 130.6, 130.0, 129.0, 128.6, 128.5, 127.4, 126.5, 123.8, 115.7, 104.0, 79.8, 21.3.

2-amino-5-oxo-4-(m-tolyl)-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile ***(5c)***[9]:
white solid (yield:237 mg, 72%). ^{1}H NMR (400 MHz, DMSO) δ 8.23 (s, 1H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 7.2 Hz, 2H), 6.92 (s, 1H), 6.82 (s, 2H), 4.19 (s, 1H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 165.7, 164.8, 131.2, 152.1, 145.6, 130.6,130.0, 129.0, 128.6, 128.5, 127.4, 126.5, 123.8, 115.7, 104.0, 79.8, 21.3.

2-amino-4-(4-methoxyphenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile ***(5d)***[8]:
white solid (yield:284 mg, 82%). ^{1}H NMR (400 MHz, DMSO) δ 8.41 (s, 2H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.03 (d, *J* = 7.2 Hz, 2H), 4.18 (s, 1H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 163.5, 158.3, 156.7, 152.1, 150.9, 142.0, 127.2, 26.3, 125.4, 123.4, 122.6, 121.2, 115.3, 114.6, 102.7, 56.7, 49.7.

2-amino-4-(2,3-dimethoxyphenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile ***(5e)***[9]:
white solid (yield:293 mg, 78%). ^{1}H NMR (400 MHz, DMSO) δ 8.45 (s, 2H), 7.88 – 7.43 (m, 2H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.06 (d, *J* = 7.2 Hz, 3H), 3.86 (s, 1H), 3.65 (s, 3H), 3.38 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 167.3, 166.4, 132.8, 153.7, 147.2, 132.2, 131.6, 130.6, 130.2, 130.1, 129.0, 128.1, 125.4, 125.4 117.3, 105.6, 81.4, 31.6, 22.9.

2-amino-5-oxo-4-(2,3,4-trimethoxyphenyl)-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile ***(5f)***:
white solid (yield:312 mg, 77%). ^{1}H NMR (400 MHz, DMSO) δ 8.36 (s, 2H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.36 – 7.27 (m, 2H), 7.98 (d, *J* = 7.2 Hz, 2H), 3.80 (s, 1H), 3.71 – 3.54 (m, 9H). ^{13}C NMR (100 MHz, DMSO) δ 159.5, 158.0, 153.4 125.7, 152.0, 136.6, 132.6, 124.3, 122.5, 119.1, 116.3, 112.8, 104.8, 103.6, 59.8, 57.8, 55.7. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{18}N_2O_6$: 407.1243; observed: 407.1244.

2-amino-4-(4-chlorophenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile ***(5g)***[8]:
white solid (yield:263 mg, 75%). ^{1}H NMR (400 MHz, DMSO) δ 8.41 (s, 2H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 7.2 Hz, 2H), 4.37 (s, 1H). ^{13}C NMR (100 MHz, DMSO) δ 164.4, 162.1, 160.0, 156.4, 151.0, 147.2, 139.0, 132.0, 129.5, 128.3, 125.5, 123.7, 120.9, 119.9, 113.9, 112.9, 82.2, 42.9.

2-amino-4-(4-chlorophenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile ***(5h)***[9]:
white solid (yield:213 mg, 61%). ^{1}H NMR (400 MHz, DMSO) δ 8.40 (s, 2H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 7.2 Hz, 2H), 4.18 (s, 1H). ^{13}C NMR (100 MHz, DMSO) δ 165.7, 164.8, 161.2, 152.1, 145.6, 130.6, 130.0, 129.0, 128.5, 127.4, 126.5, 123.8, 115.7, 104.0, 79.8 58.1.

2-amino-4-(2,5-dichlorophenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile ***(5i)***[9]:
white solid (yield:243 mg, 63%). ^{1}H NMR (400 MHz, DMSO) δ 7.92 (d, *J* = 7.2 Hz, 1H), 7.73 (t, 1H), 7.53 – 7.46 (m, 6H), 7.37 – 7.35 (m, 1H), 5.00 (s, 1H). ^{13}C NMR (100 MHz, DMSO) δ 159.4, 158.1, 154.3, 152.2, 133.0, 132.1, 131.2, 131.1, 128.7, 124.6, 122.5, 118.6, 116.5, 112.8, 101.9, 55.7.

N-(4-(2-amino-3-cyano-5-oxo-4H,5H-pyrano[3,2-c]chromen-4-yl)phenyl)acetamide ***(5j)***:
white solid (yield:205 mg, 60%). ^{1}H NMR (400 MHz, DMSO) δ 8.06 (s, 2H), 7.81 (d, J = 7.2 Hz, 2H), 7.63 (t, 2H), 7.37 (s, 2H), 7.33 (d, J = 7.2 Hz, 4H), 5.60 (s, 1H). ^{13}C NMR (100 MHz, DMSO) δ 165.6, 162.0, 153.4, 132.7, 123.9, 123.1, 116.3, 115.7, 90.8. HRMS (ESI) m/z: HRMS (ESI) m/z: [M-H]$^+$ calculated for $C_{20}H_{11}N_3O_3$: 340.0722; observed: 340.0733.

N-(4-(2-amino-3-cyano-5-oxo-4H,5H-pyrano[3,2-c]chromen-4-yl)phenyl)acetamide ***(5k)***:
white solid (yield:250 mg, 67%). ^{1}H NMR (400 MHz, DMSO) δ 11.38 (s, 1H), 10.11 (s, 1H), 8.16 (s, 2H), 7.96 (d, J = 7.2 Hz, 3H), 7.73 (d, J = 7.2 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 3.40 (s, 1H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 177.6, 168.5, 142.0, 140.7, 128.7, 127.9, 118.6, 24.0. HRMS (ESI) m/z: [M+H]$^+$ calculated for $C_{21}H_{15}N_3O_4$: 374.1141; observed: 374.1148.

2-amino-7,7-dimethyl-4-(naphthalen-2-yl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(5l)***:
white solid (yield:223 mg, 67%). ^{1}H NMR (400 MHz, DMSO) δ 8.33 (d, J = 7.2 Hz, 2H), 7.85 (d, J = 7.2 Hz, 2H), 7.69 (d, J = 7.2 Hz, 2H), 7.49 – 7.35 (m, 2H), 7.17 (d, J = 7.2 Hz, 2H), 6.93 (s, 4H), 5.10 (s, 1H). ^{13}C NMR (100 MHz, DMSO) δ 194.5, 194.5, 161.5, 157.2, 132.1, 129.5, 127.1, 125.7, 124.6, 124.4, 124.3, 122.4, 118.4, 118.4, 112.2, 57.7, 57.6, 48.8. HRMS (ESI) m/z: [M+H]$^+$ calculated for $C_{25}H_{16}N_2O_3$: 393.1239; observed: 393.1224.

NMR spectrum of the catalytic isolated products

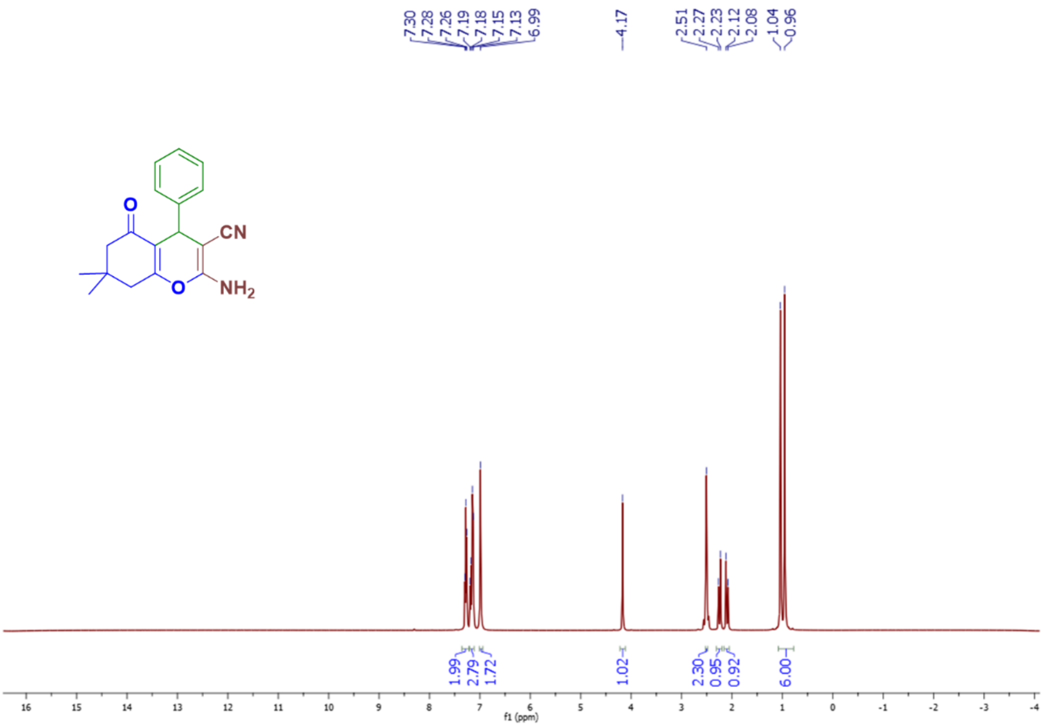

Figure S16. ^{1}H NMR spectrum **4a** in DMSO-d_6 (400 MHz, 293 K).

Supporting Information

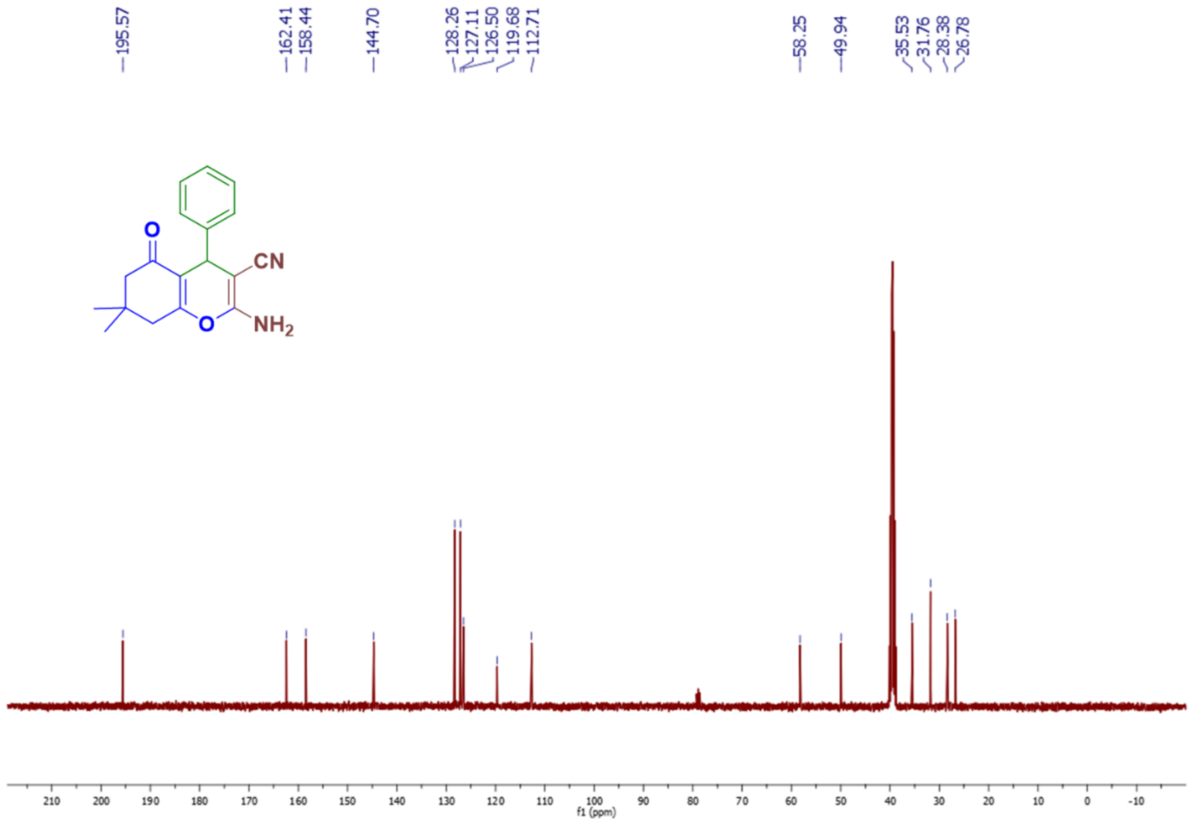

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **4a** in DMSO-d_6 (100 MHz, 293 K).

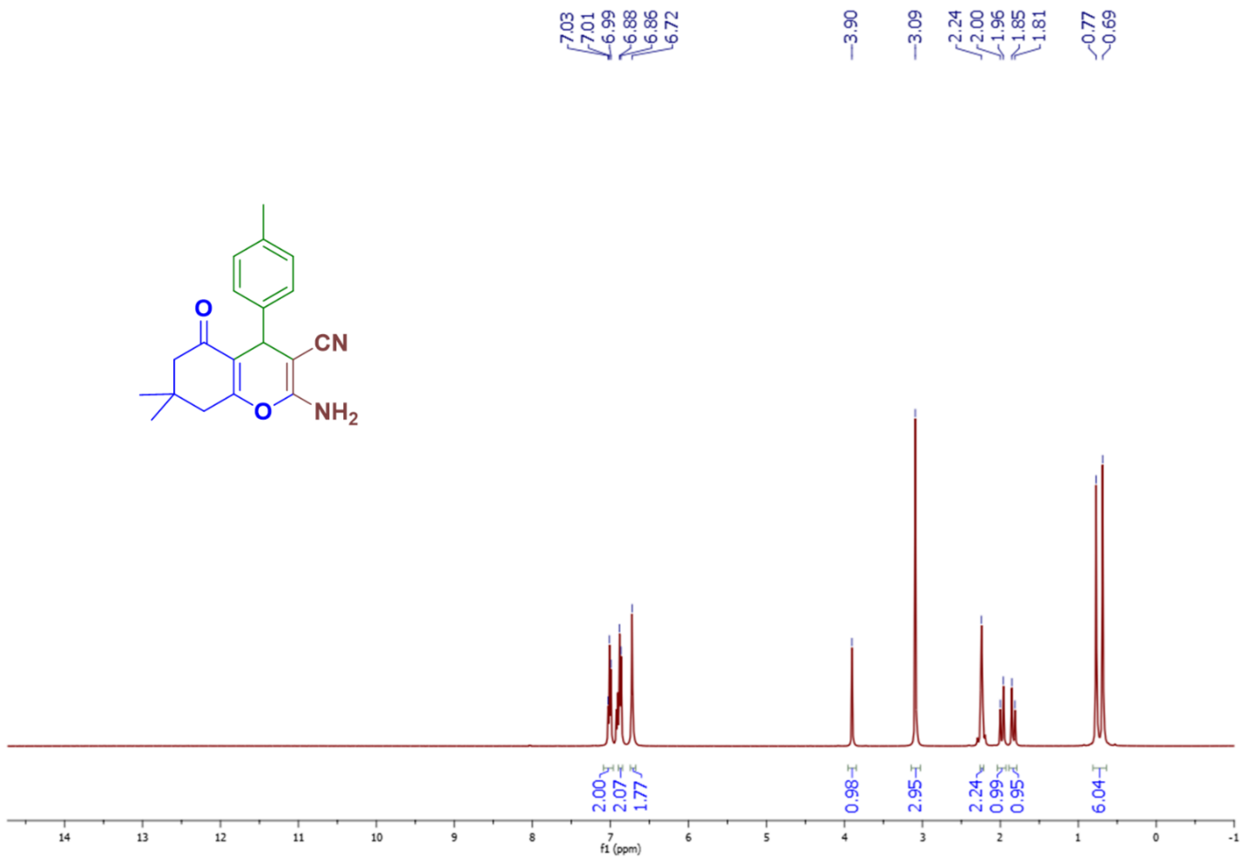

Figure S18. ^{1}H NMR spectrum of 4**b** in DMSO-d_6 (400 MHz, 293 K).

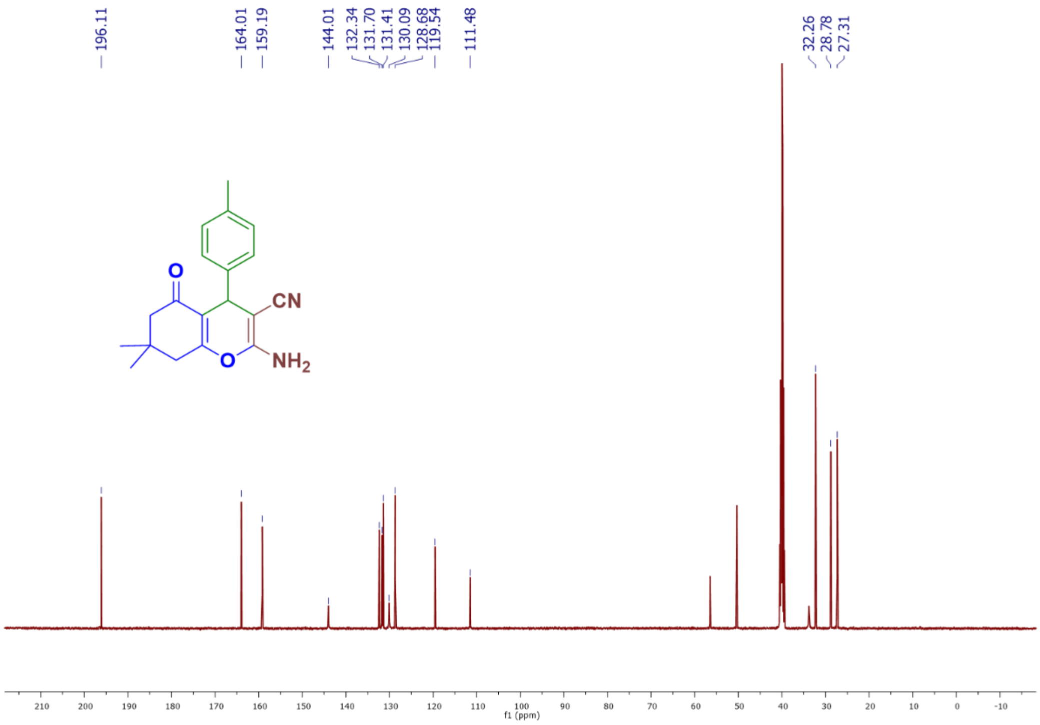

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **4b** in DMSO-d_6 (100 MHz, 293 K).

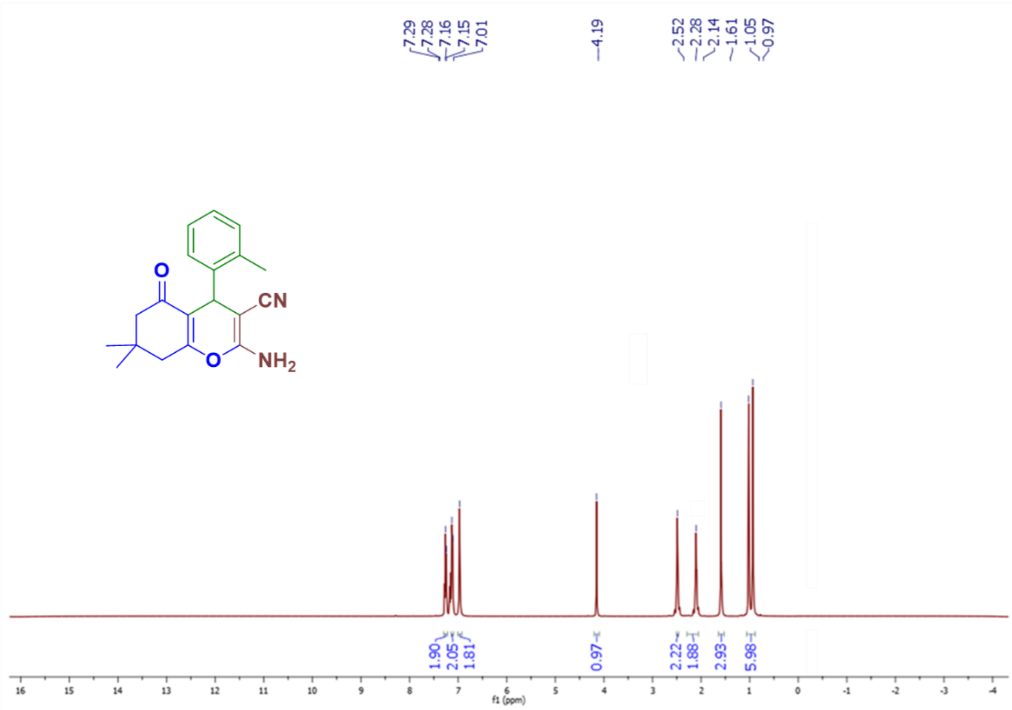

Figure S20. ^{1}H NMR spectrum **4c** in DMSO-d_6 (400 MHz, 293 K).

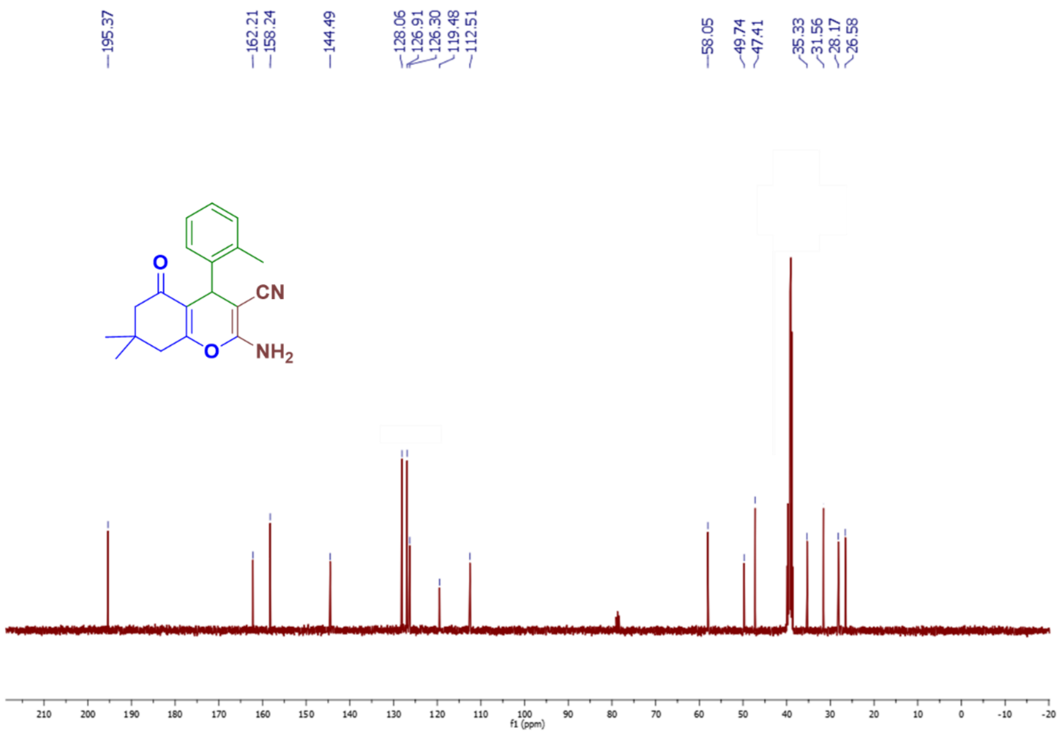

Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **4c** in DMSO-*d*$_6$ (100 MHz, 293 K).

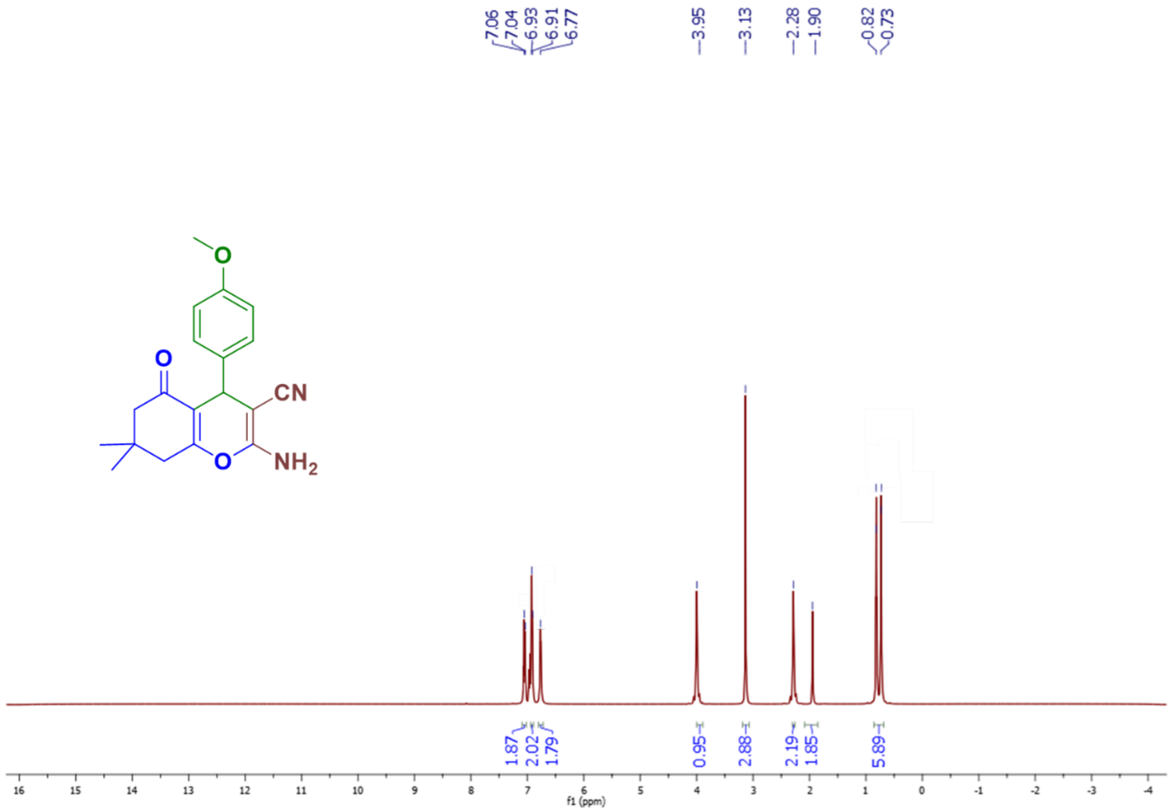

Figure S22. ^{1}H NMR spectrum of **4d** in DMSO-*d*$_6$ (400 MHz, 293 K).

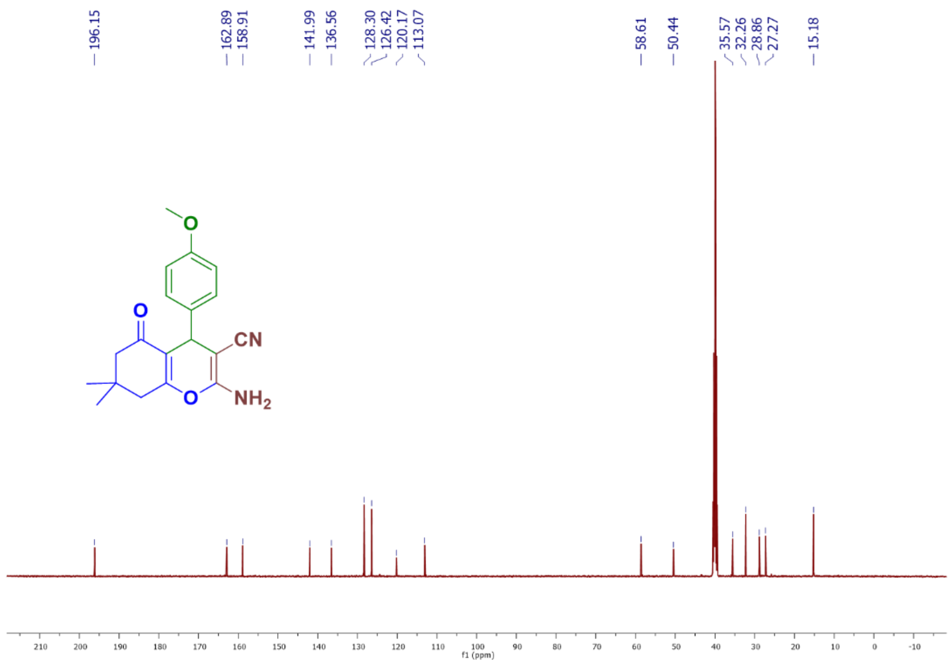

Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **4d** in DMSO-d_6 (100 MHz, 293 K).

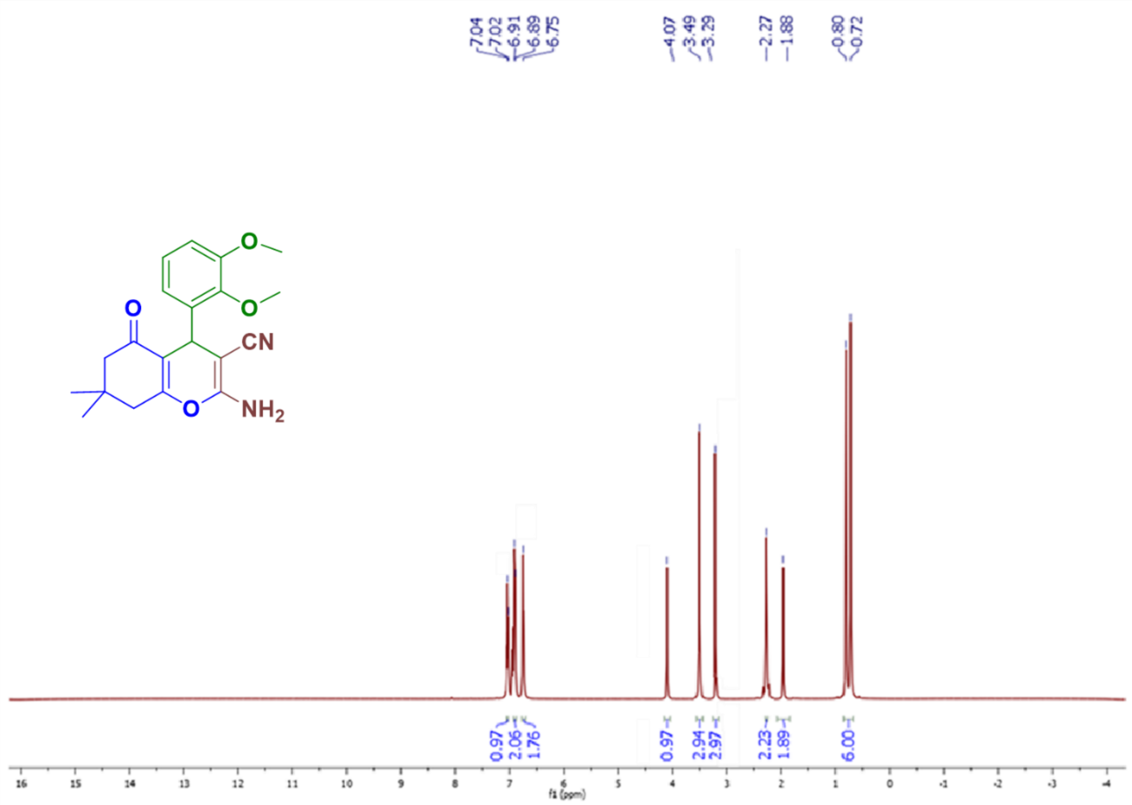

Figure S24. ^{1}H NMR spectrum **4e** in DMSO-d_6 (400 MHz, 293 K).

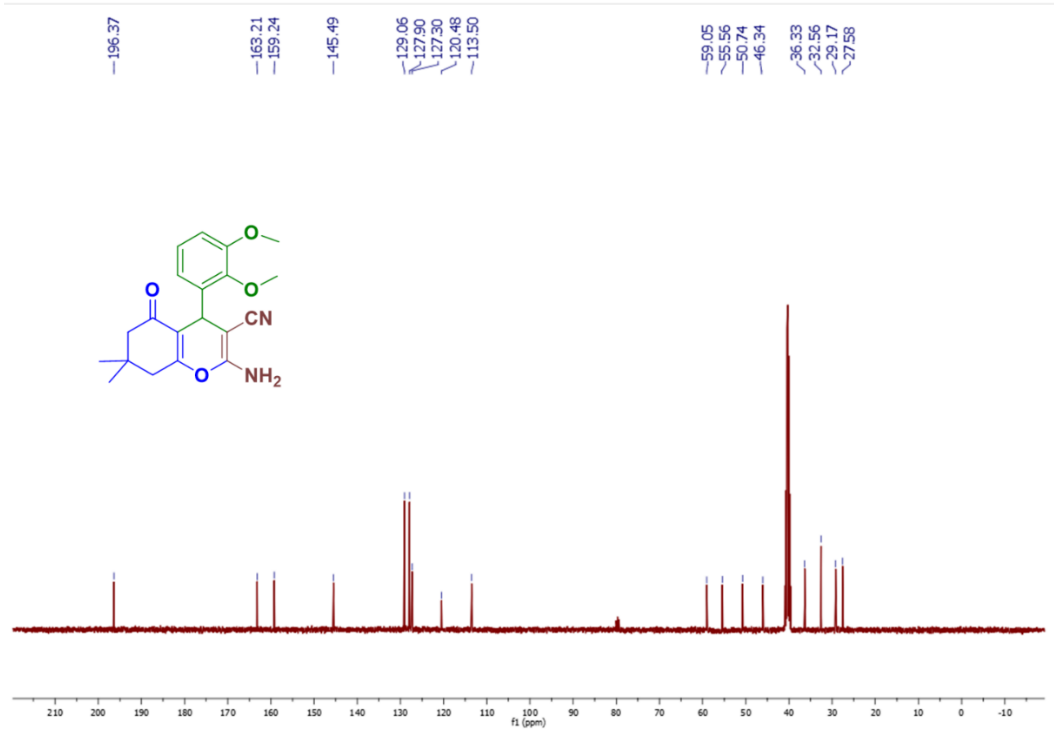

Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of **4e** in DMSO-d_6 (100 MHz, 293 K).

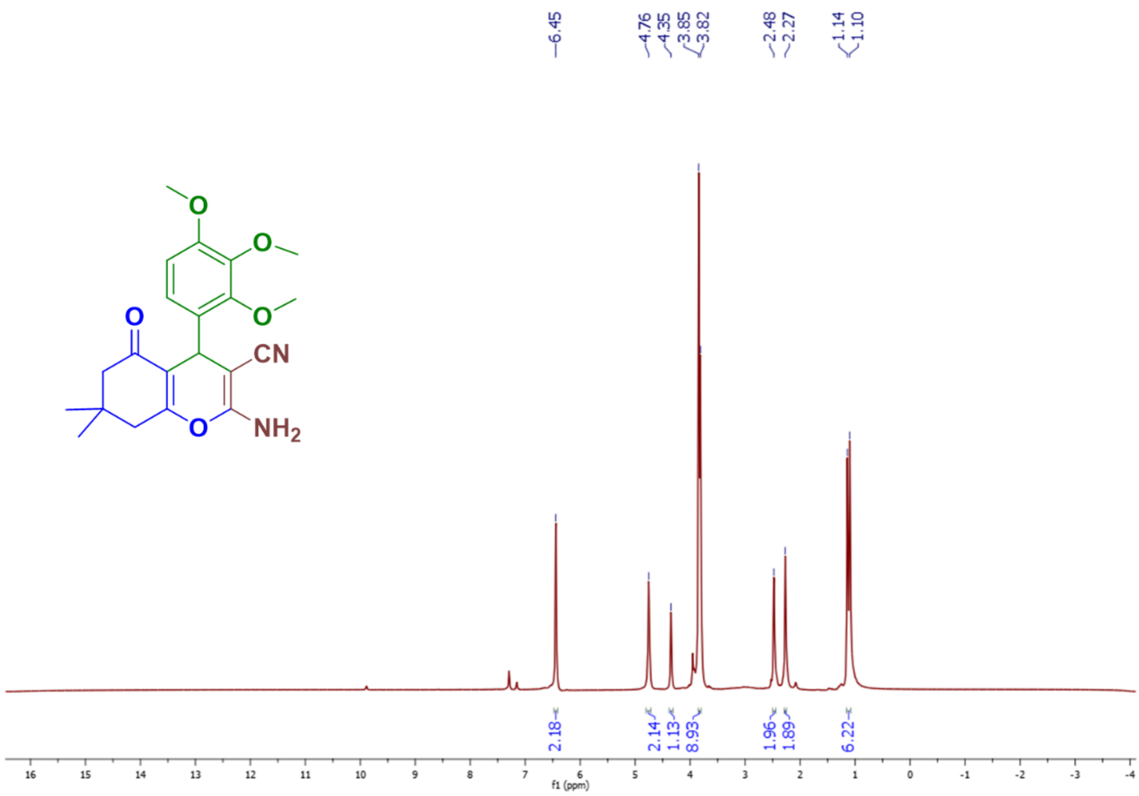

Figure S26. ^{1}H NMR spectrum of **4f** in DMSO-d_6 (400 MHz, 293 K).

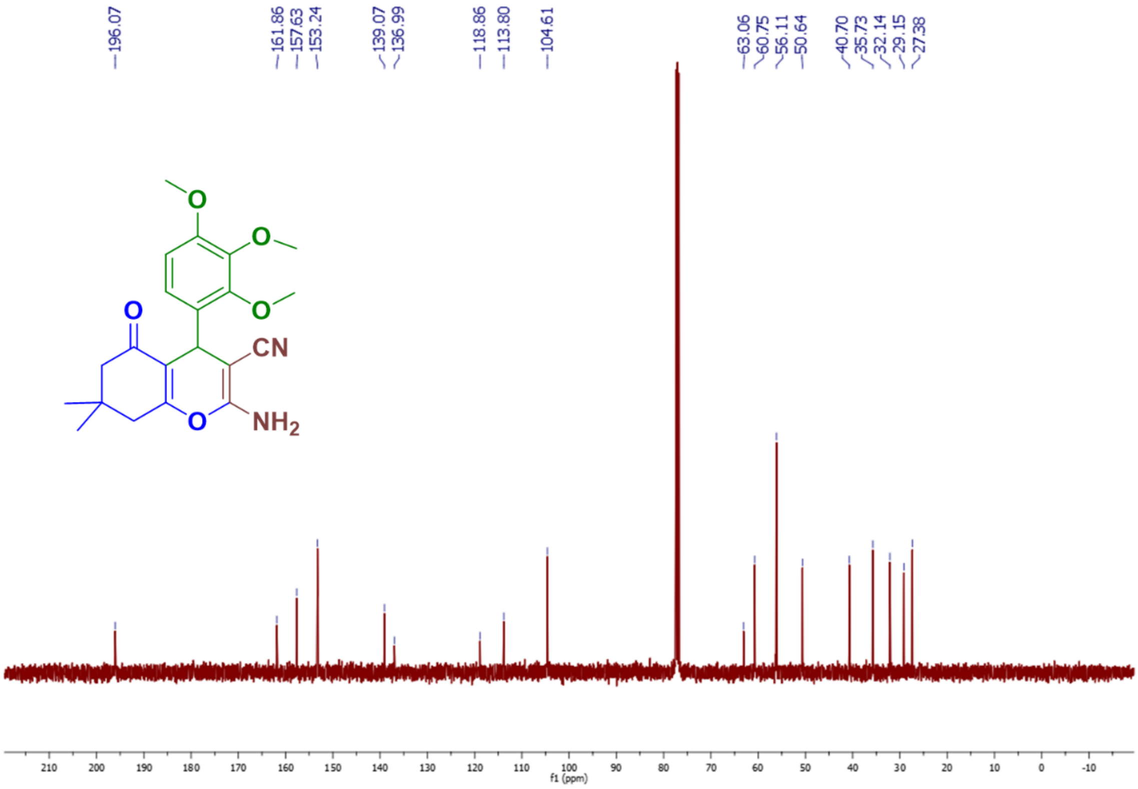

Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of **4f** in DMSO-d_6 (100 MHz, 293 K).

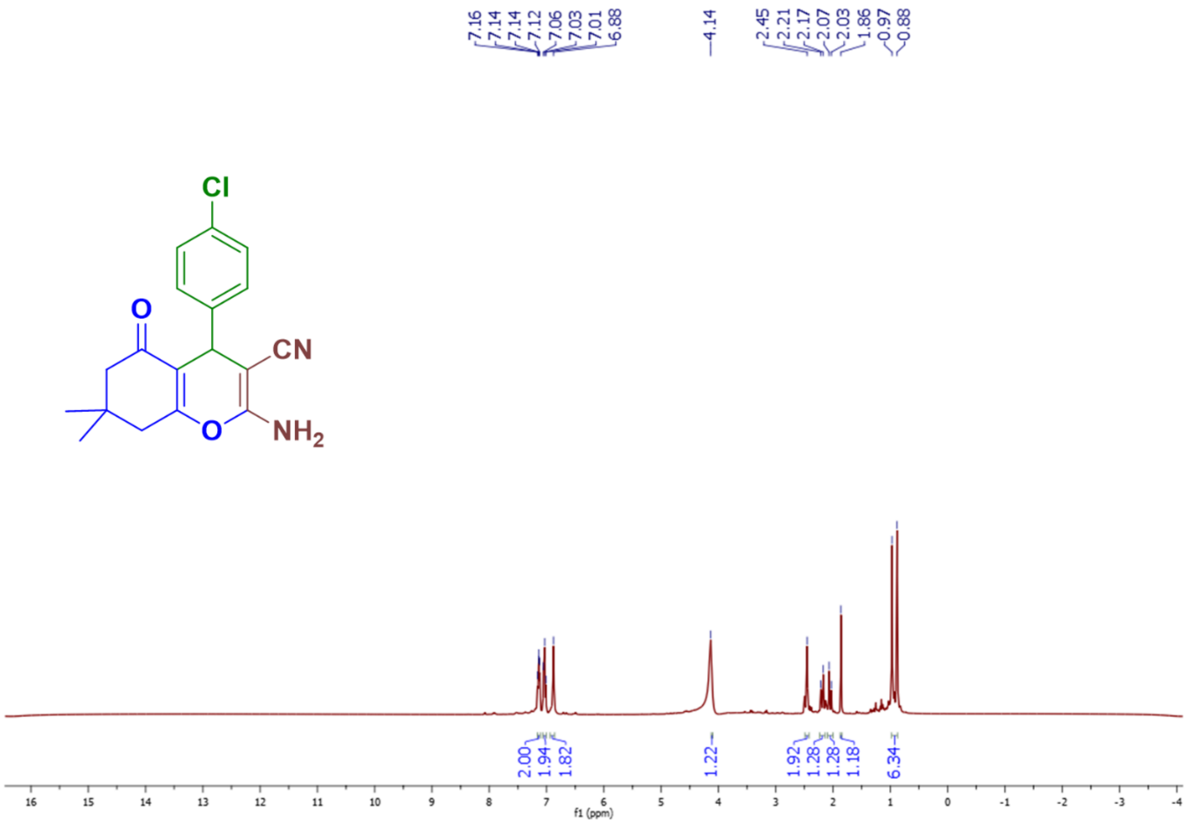

Figure S28. ^{1}H NMR spectrum **4g** in DMSO-d_6 (400 MHz, 293 K).

Supporting Information

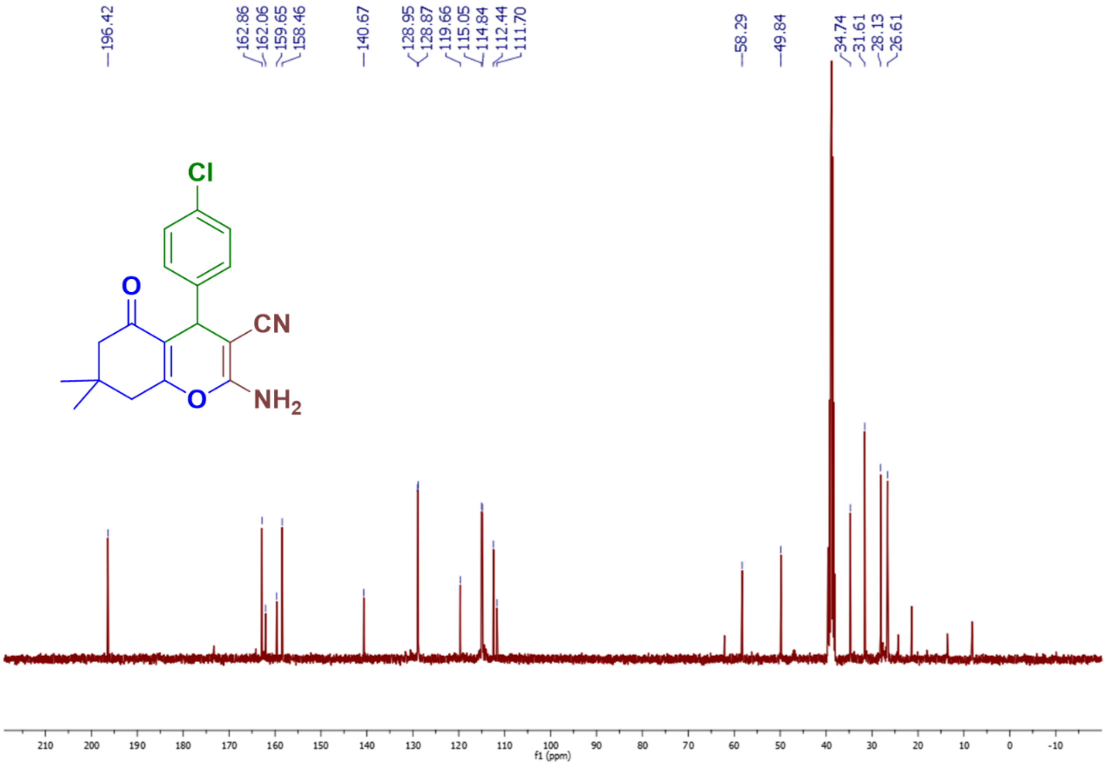

Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **4g** in DMSO-d_6 (100 MHz, 293 K).

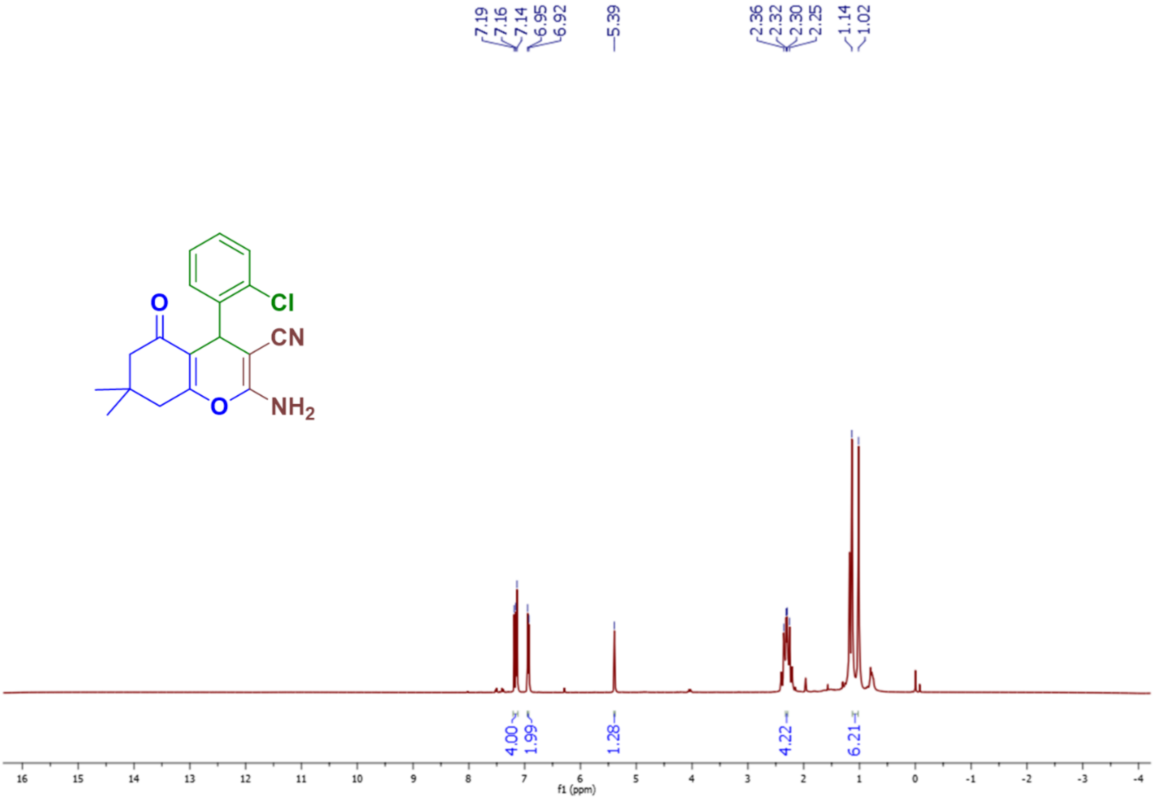

Figure S30. ^{1}H NMR spectrum of **4h** in DMSO-d_6 (400 MHz, 293 K).

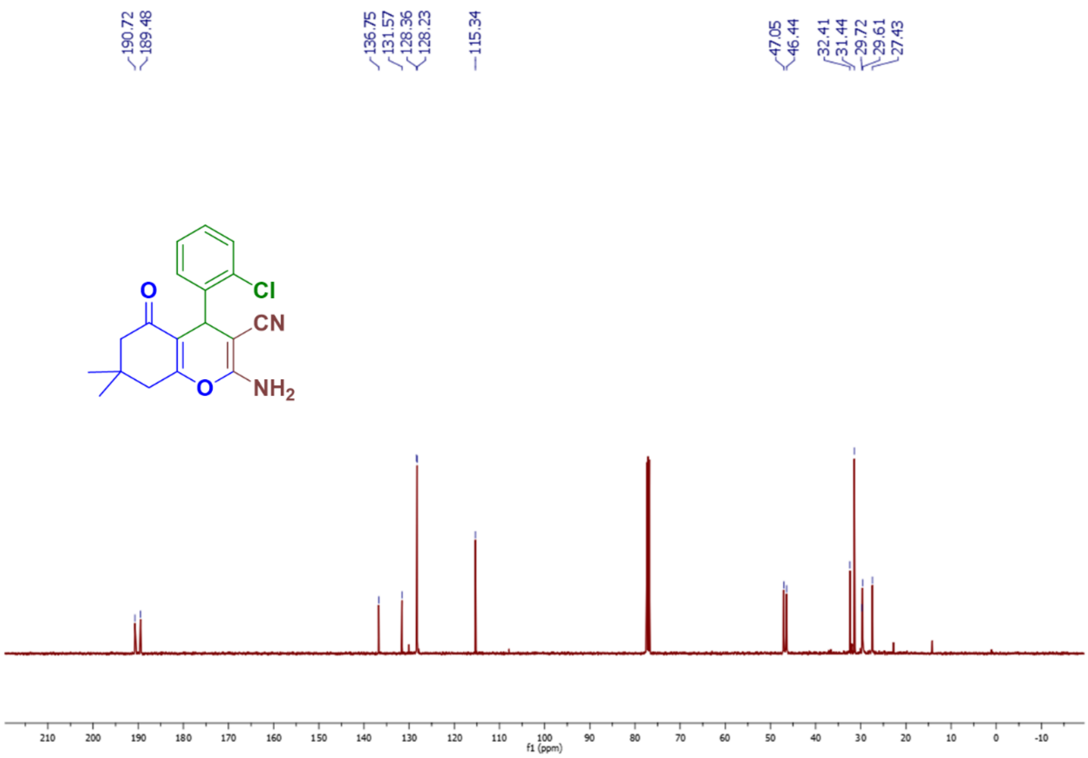

Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **4h** in DMSO-d_6 (100 MHz, 293 K).

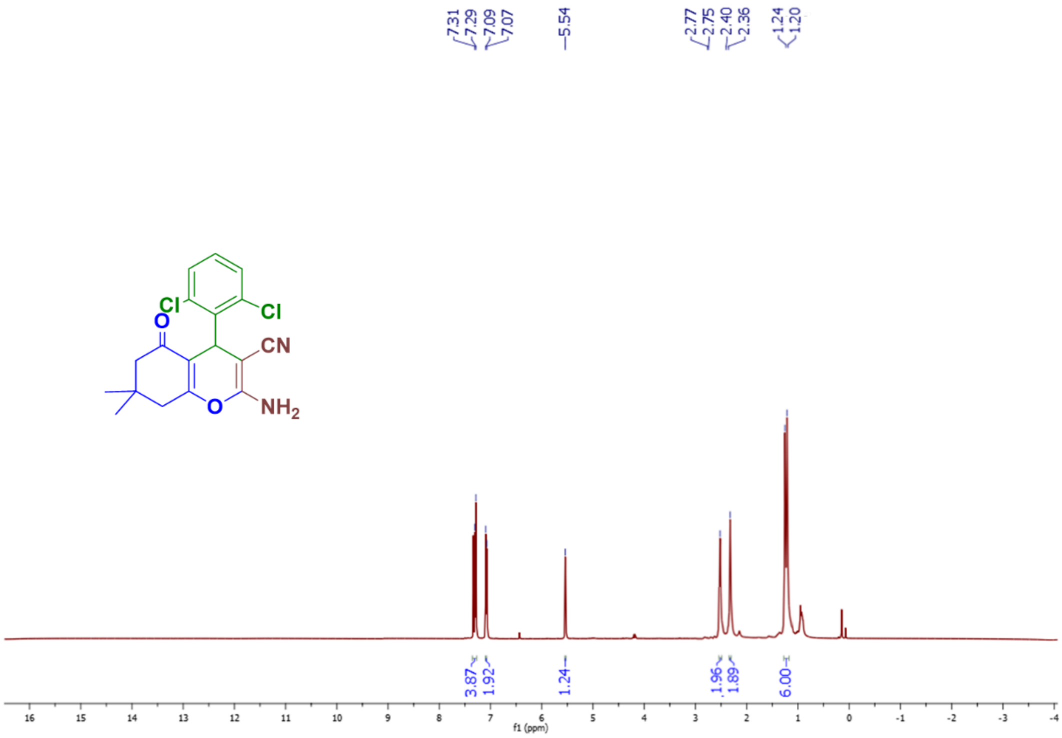

Figure S32. ^{1}H NMR spectrum **4i** in DMSO-d_6 (400 MHz, 293 K).

Supporting Information

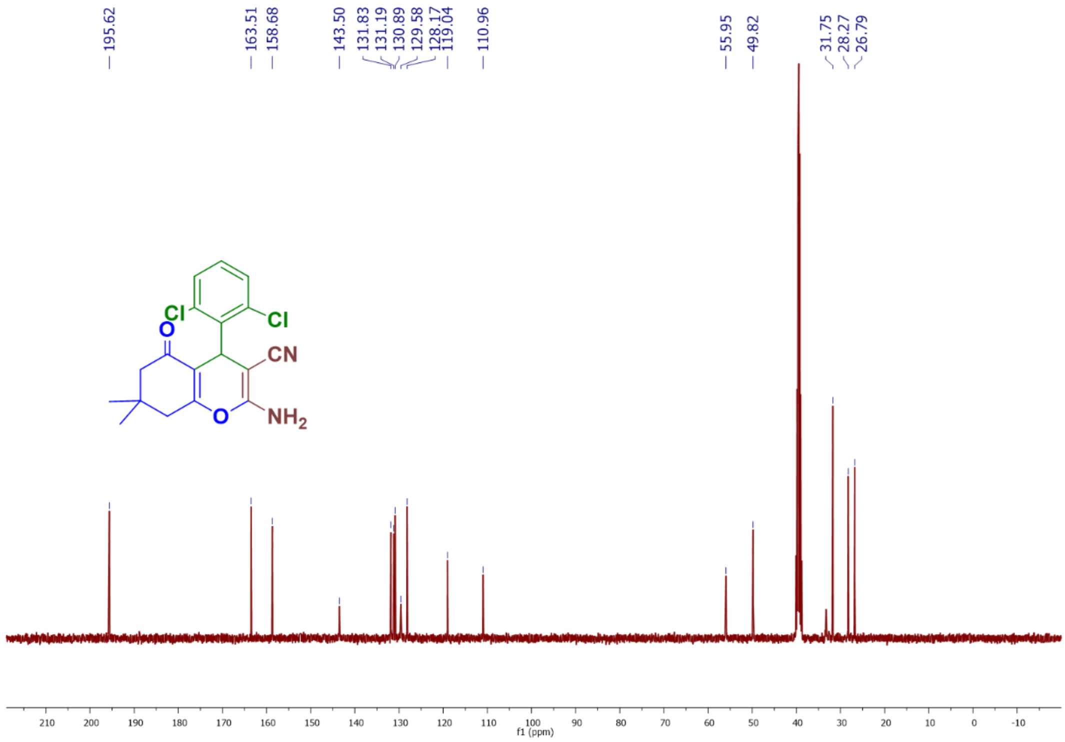

Figure S33. $^{13}C\{^1H\}$ NMR spectrum of **4i** in DMSO-d_6 (100 MHz, 293 K).

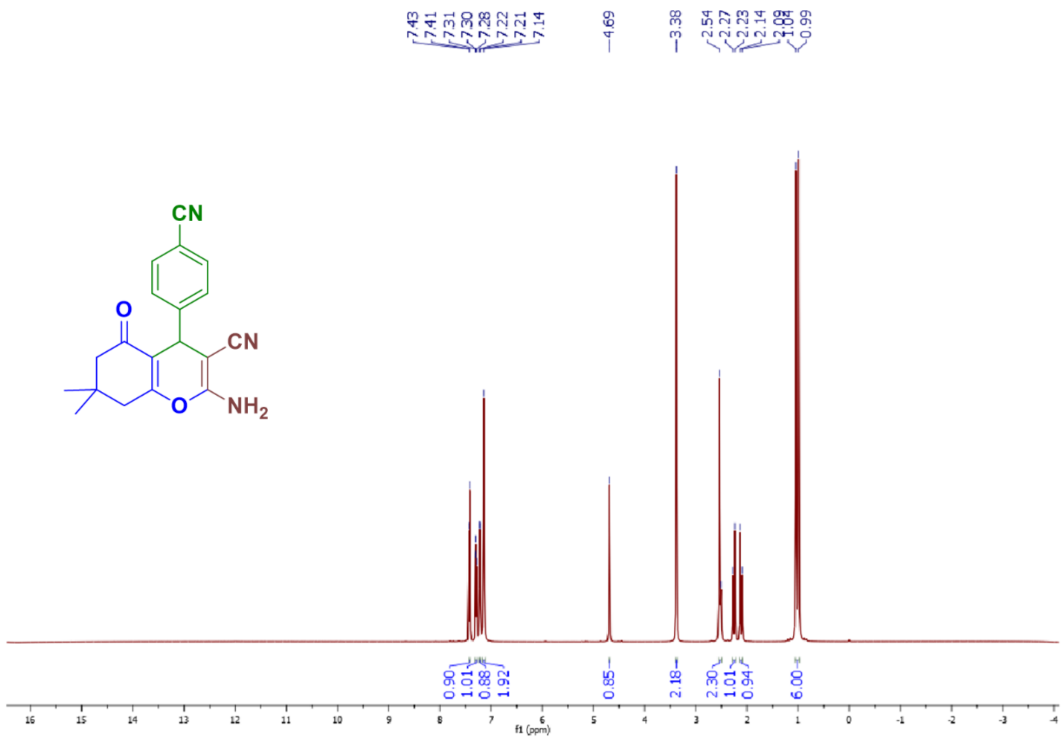

Figure S34. ^1H NMR spectrum of **4j** in DMSO-d_6 (400 MHz, 293 K).

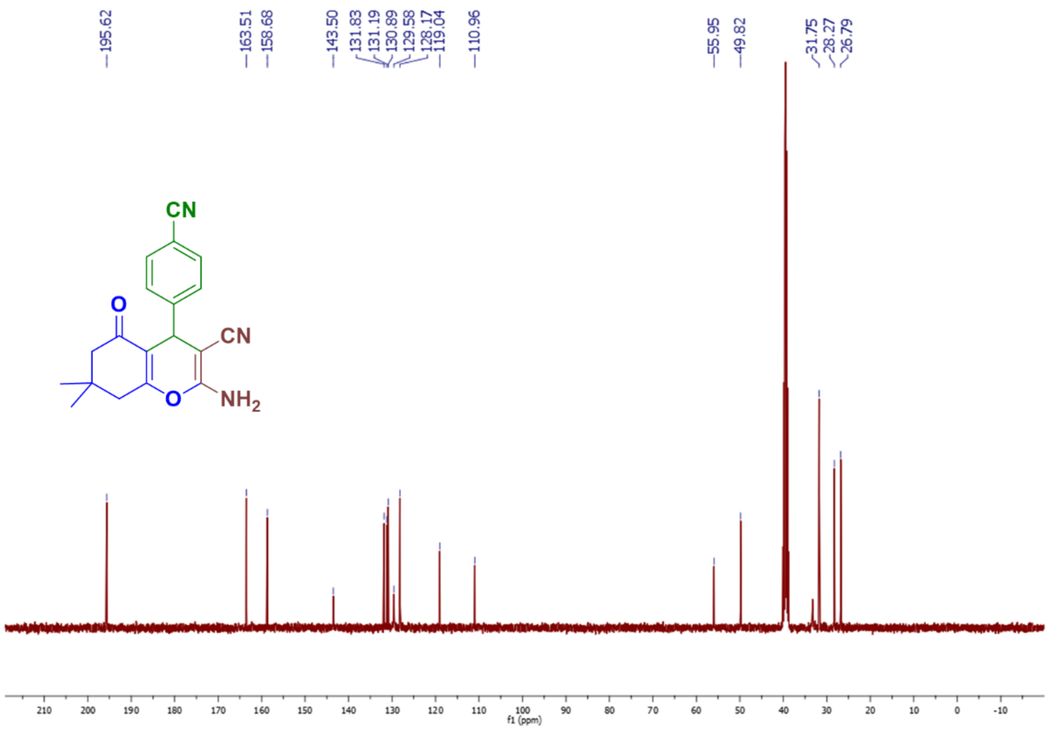

Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **4j** in DMSO-d_6 (100 MHz, 293 K).

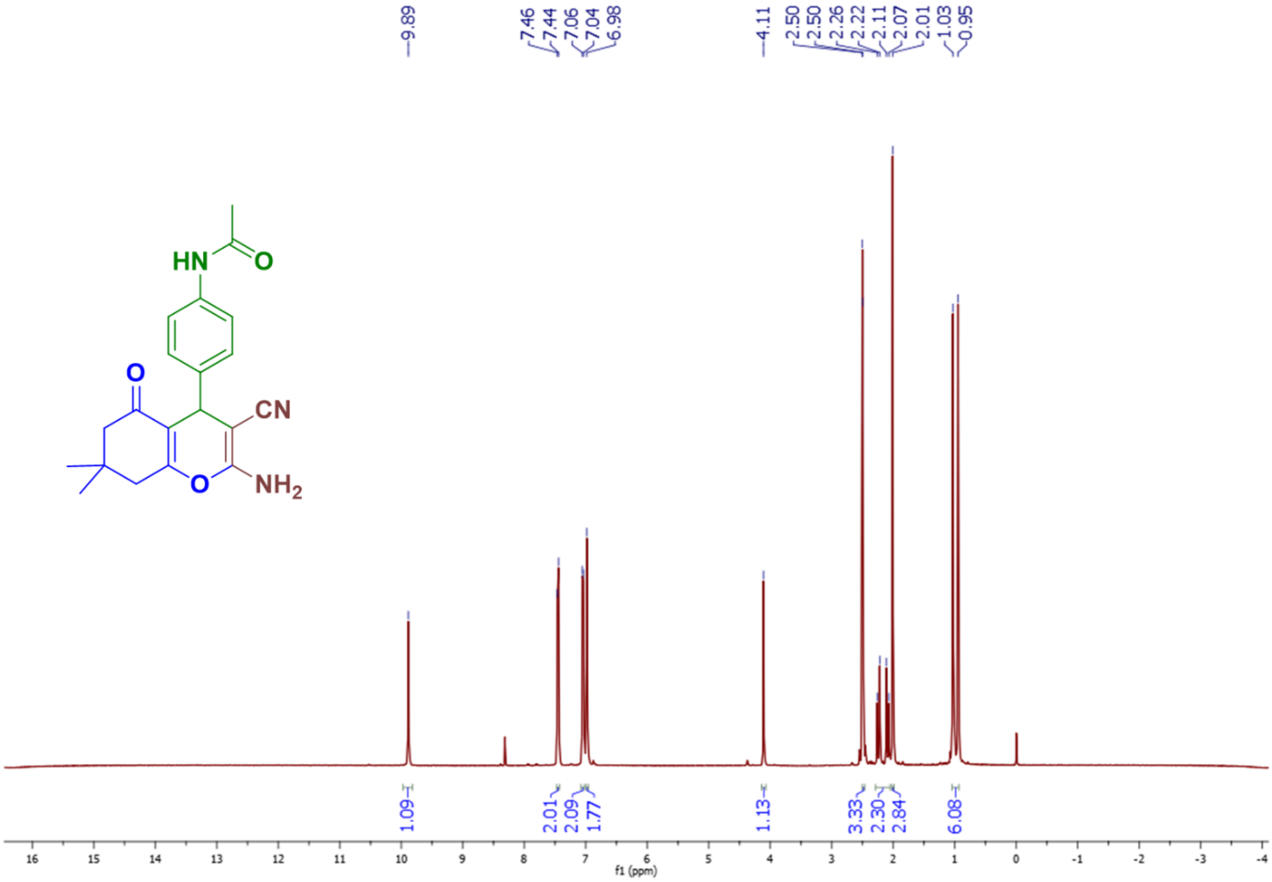

Figure S36. ^{1}H NMR spectrum **4k** in DMSO-d_6 (400 MHz, 293 K).

Supporting Information

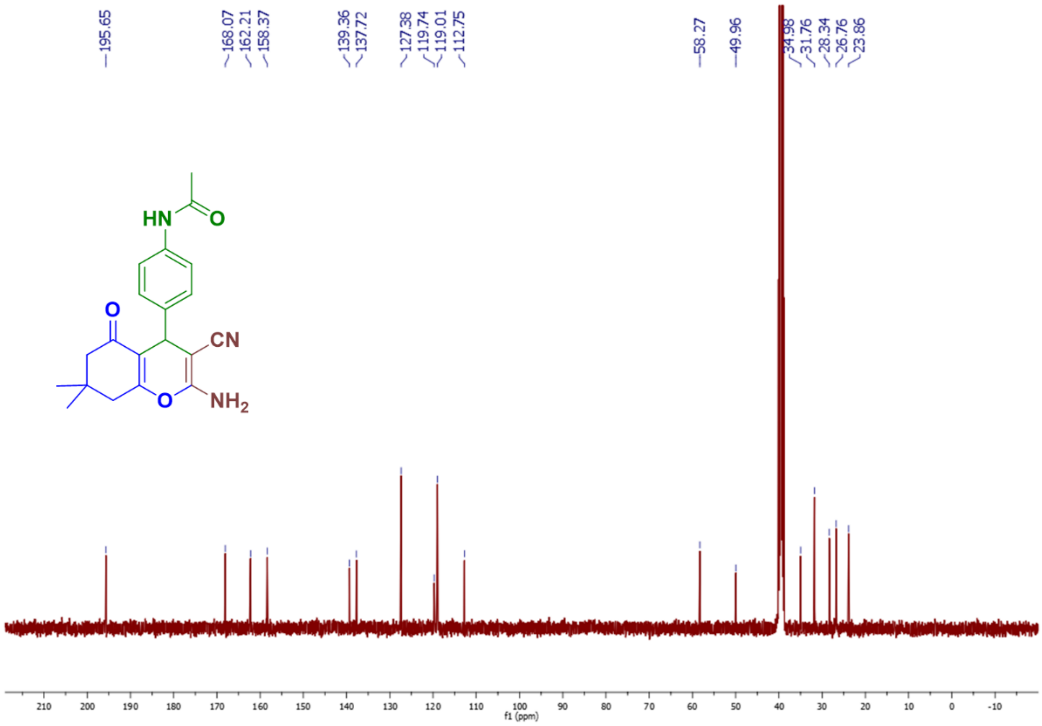

Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum of **4k** in DMSO-d_6 (100 MHz, 293 K).

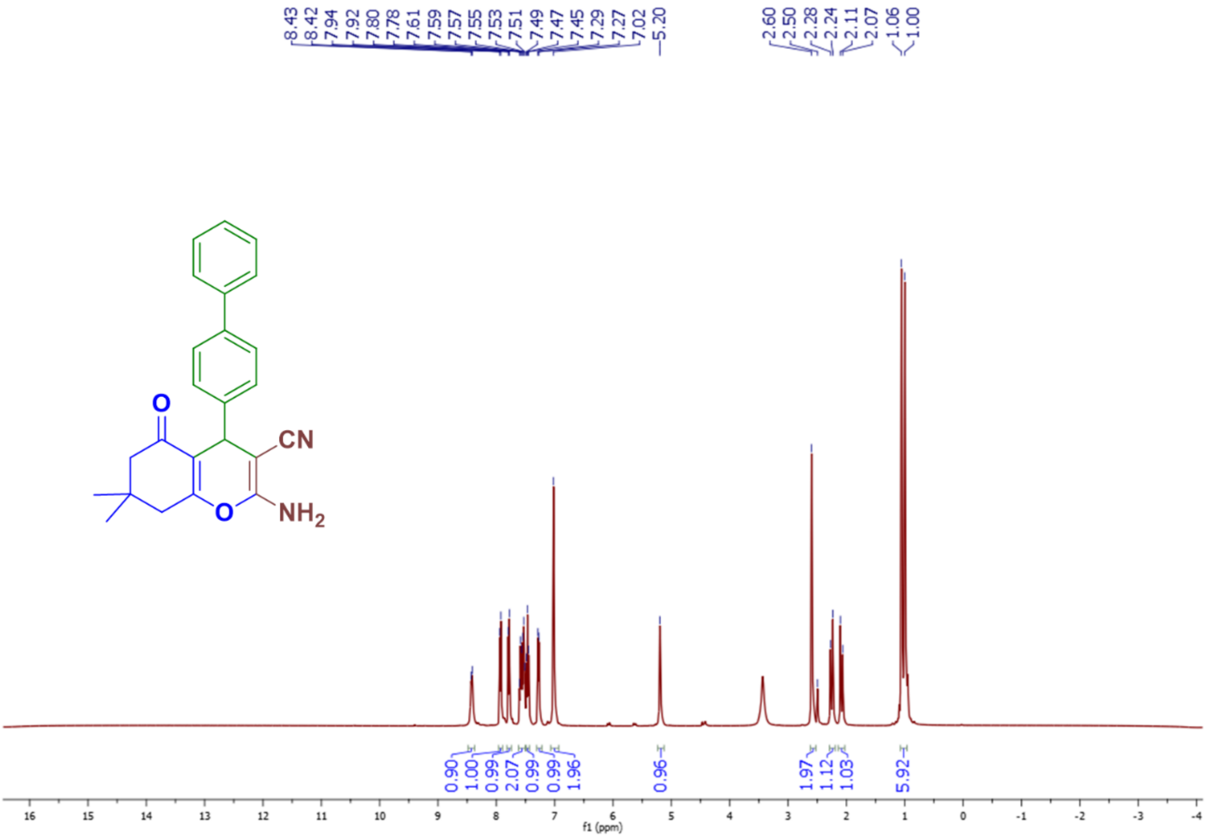

Figure S38. ^{1}H NMR spectrum of **4l** in DMSO-d_6 (400 MHz, 293 K).

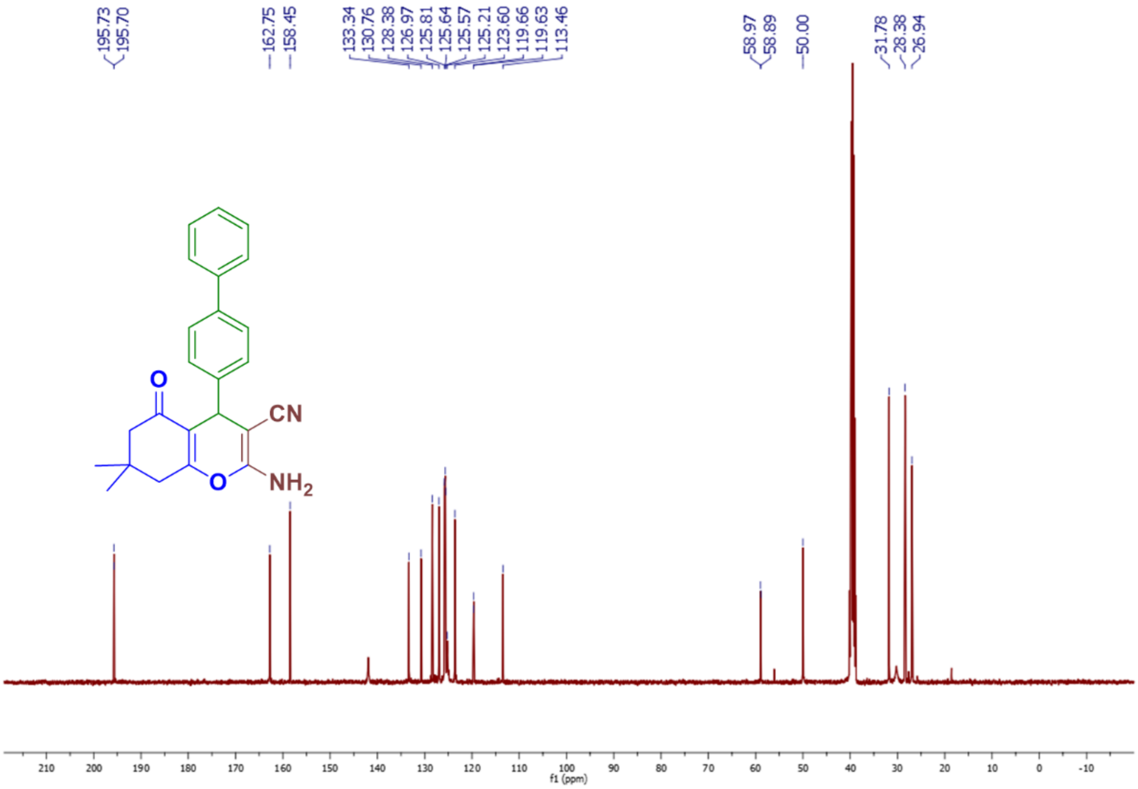

Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of **4l** in DMSO-d_6 (100 MHz, 293 K).

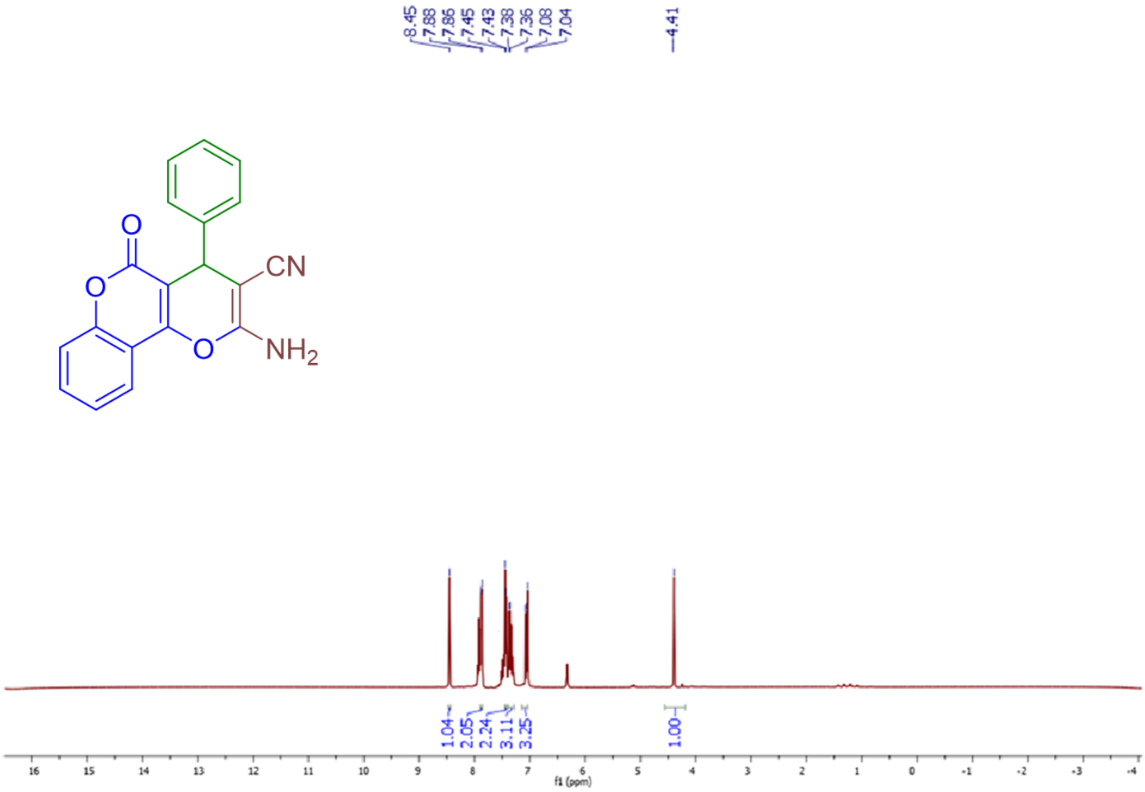

Figure S40. ^{1}H NMR spectrum **5a** in DMSO-d_6 (400 MHz, 293 K).

Supporting Information

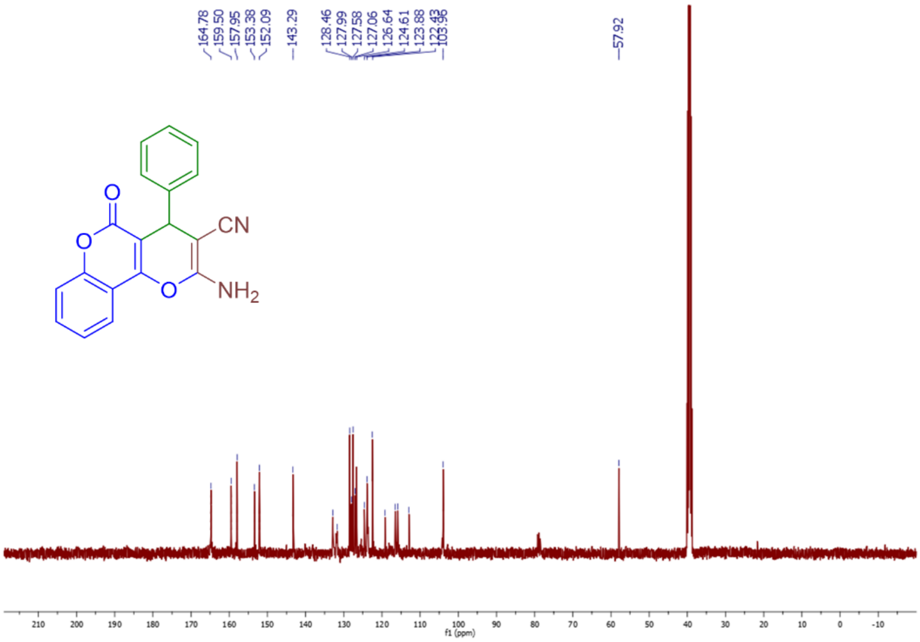

Figure S41. $^{13}C\{^1H\}$ NMR spectrum of **5a** in DMSO-d_6 (100 MHz, 293 K).

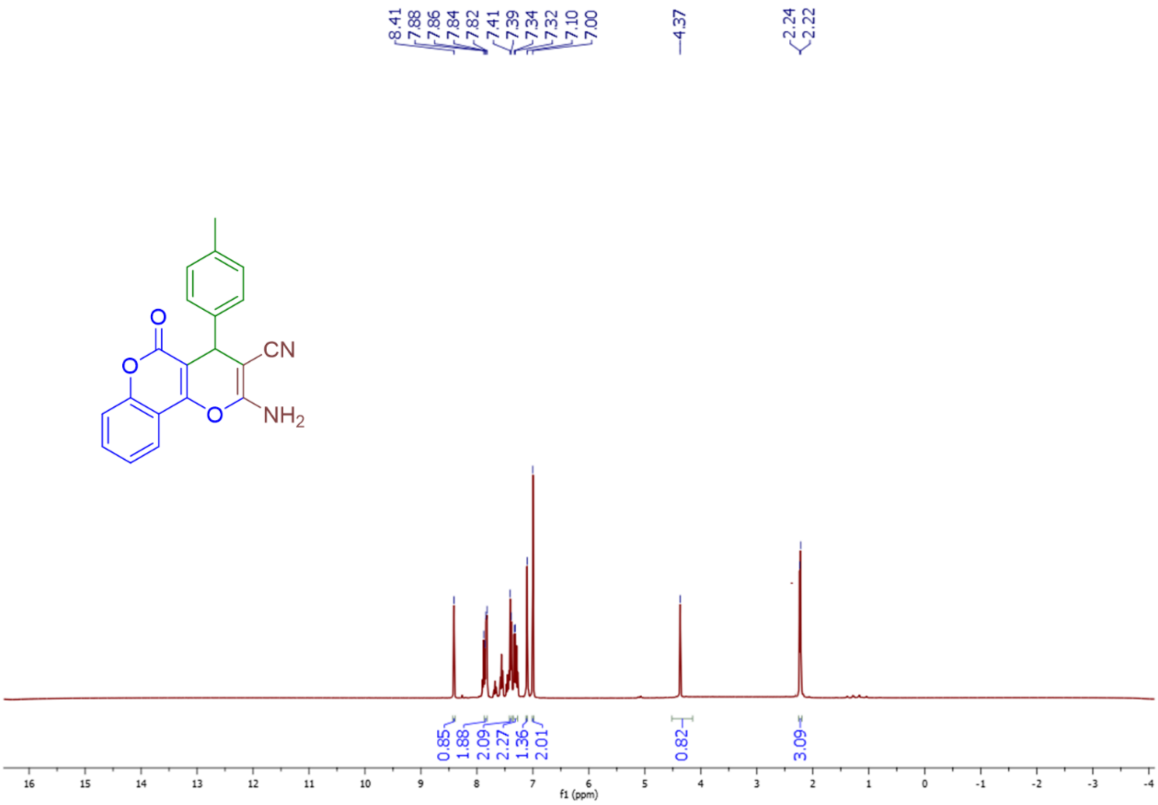

Figure S42. ^1H NMR spectrum of **5b** in DMSO-d_6 (400 MHz, 293 K).

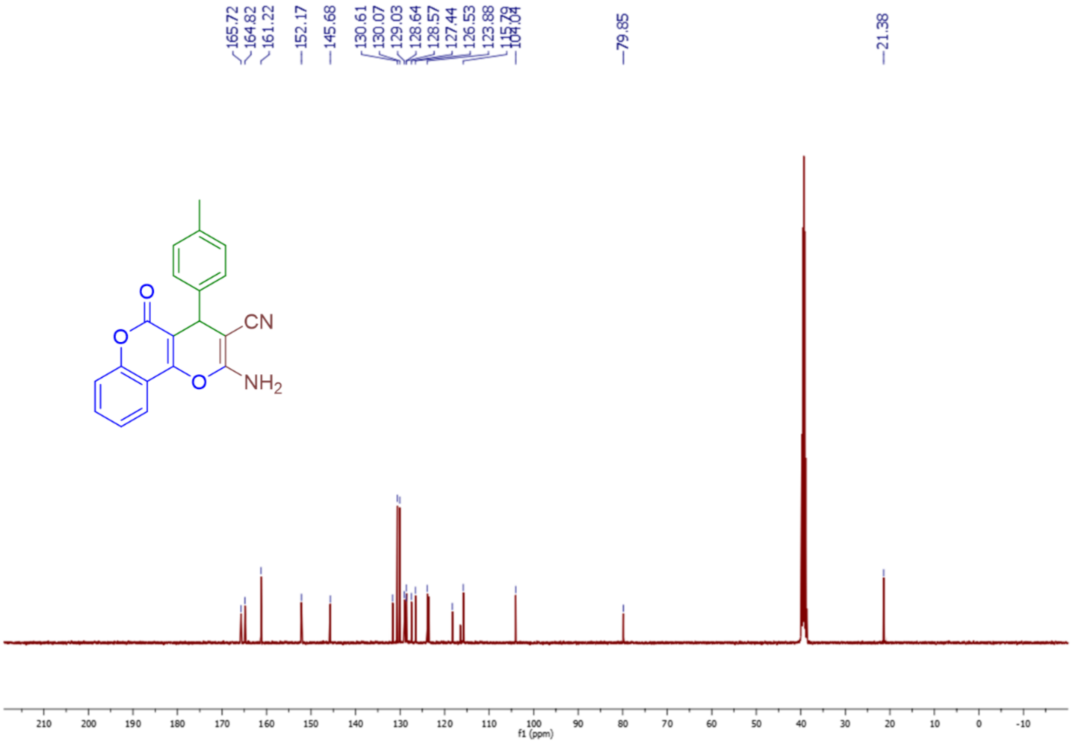

Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum of **5b** in DMSO-d_6 (100 MHz, 293 K).

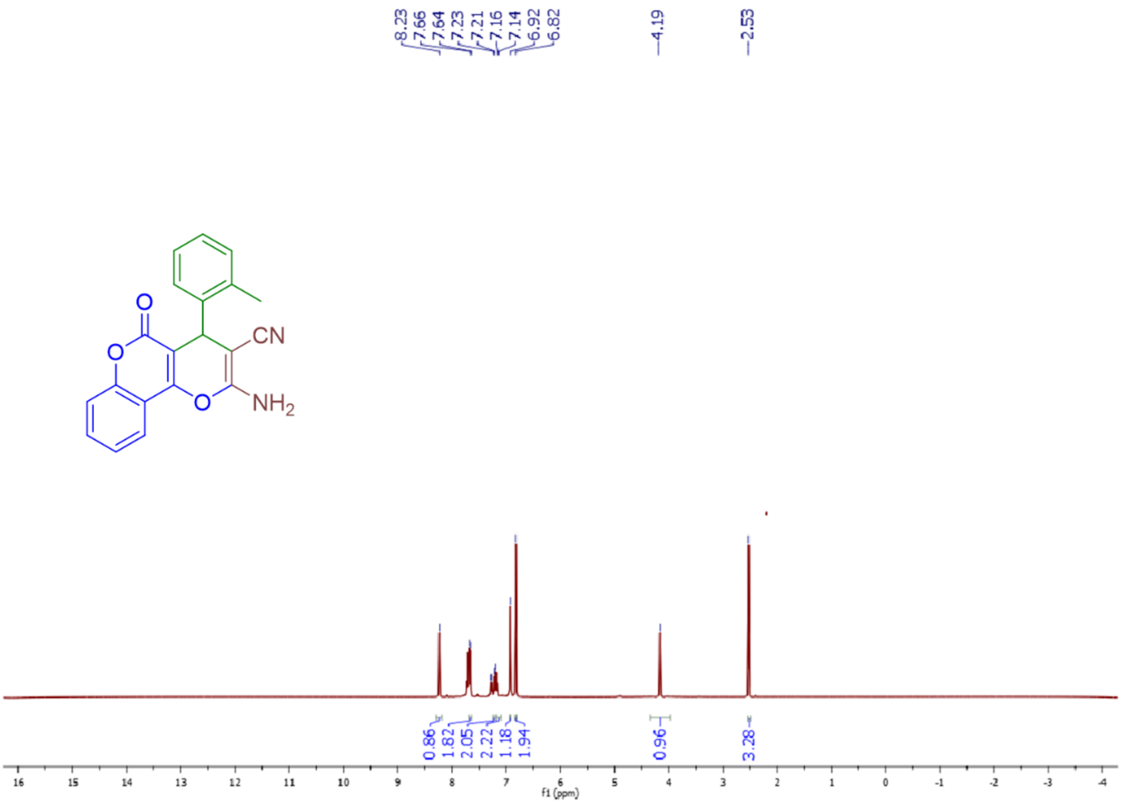

Figure S44. ^{1}H NMR spectrum **5c** in DMSO-d_6 (400 MHz, 293 K).

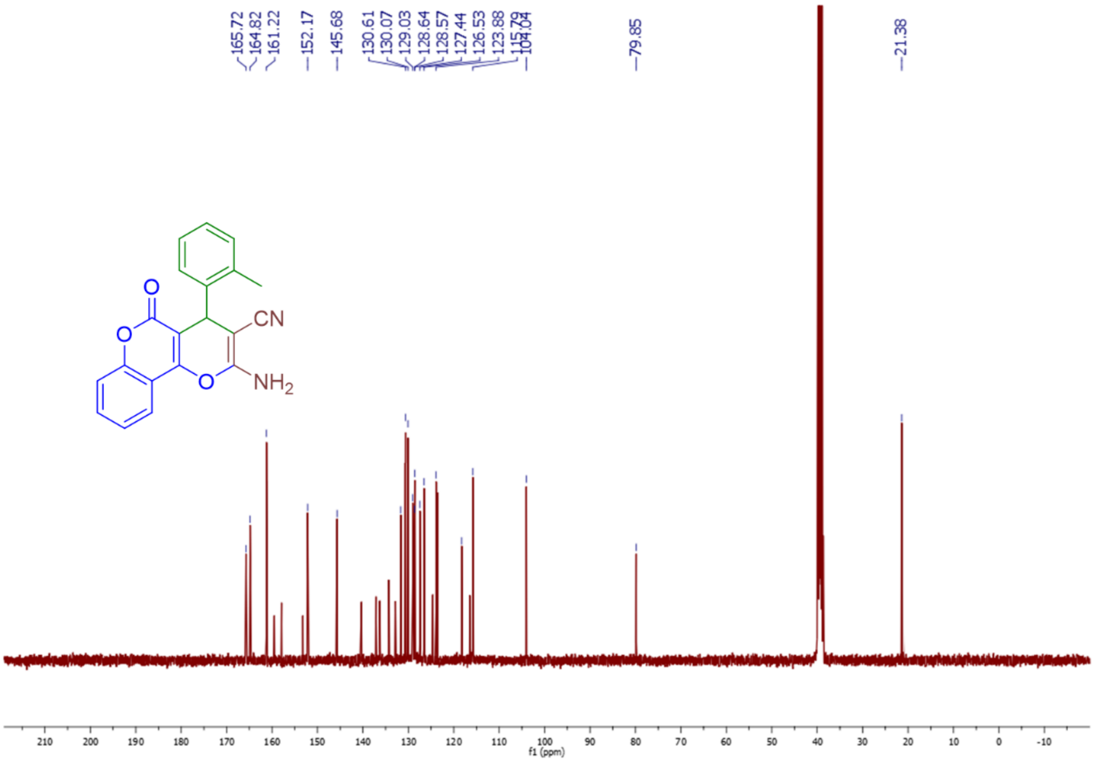

Figure S45. ${}^{13}C\{{}^{1}H\}$ NMR spectrum of **5c** in DMSO-d_6 (100 MHz, 293 K).

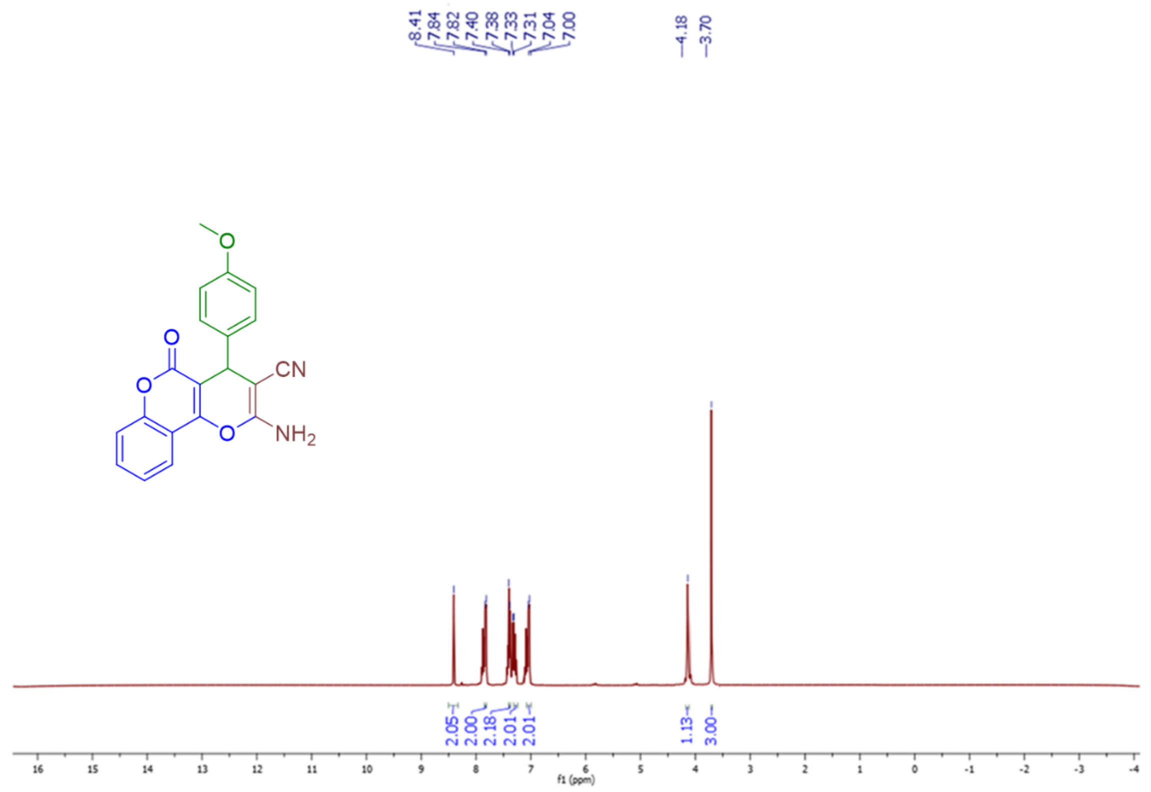

Figure S46. ${}^{1}H$ NMR spectrum of **5d** in DMSO-d_6 (400 MHz, 293 K).

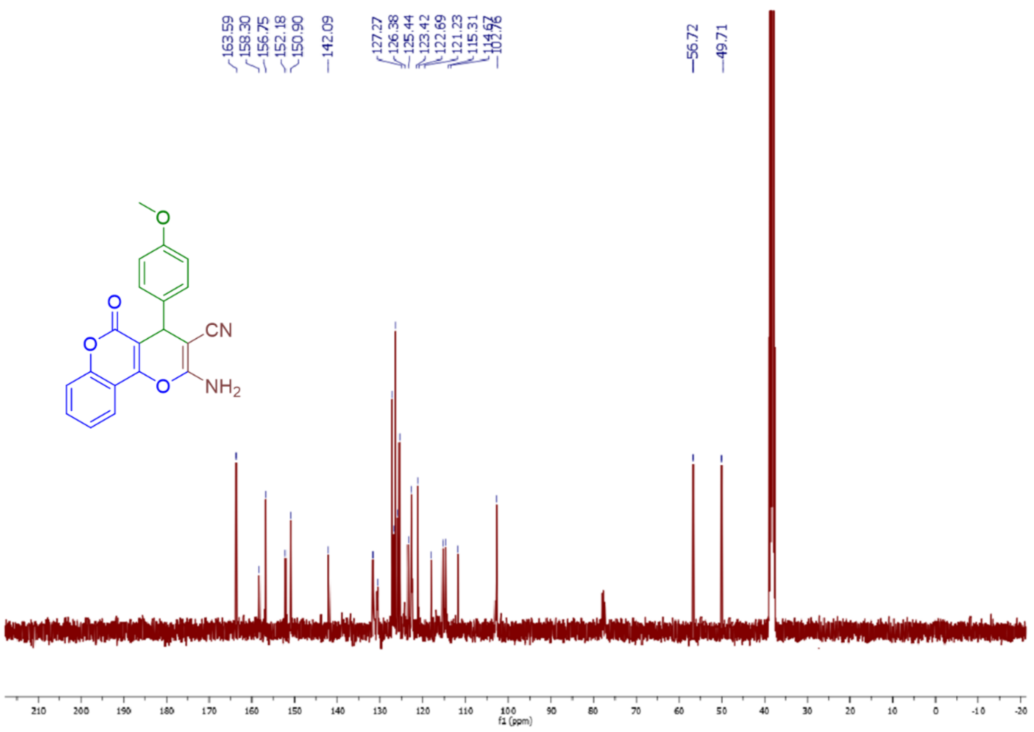

Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of **5d** in DMSO-d_6 (100 MHz, 293 K).

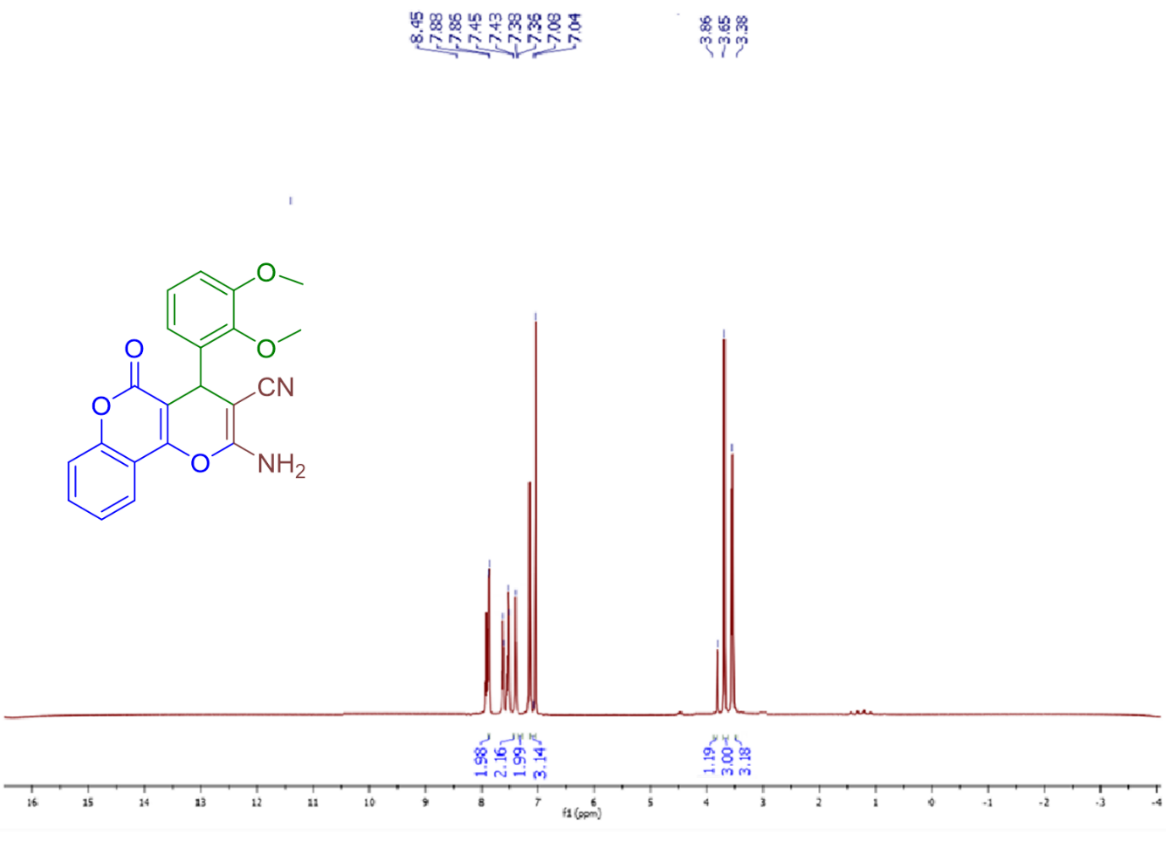

Figure S48. ^{1}H NMR spectrum **5e** in DMSO-d_6 (400 MHz, 293 K).

Supporting Information

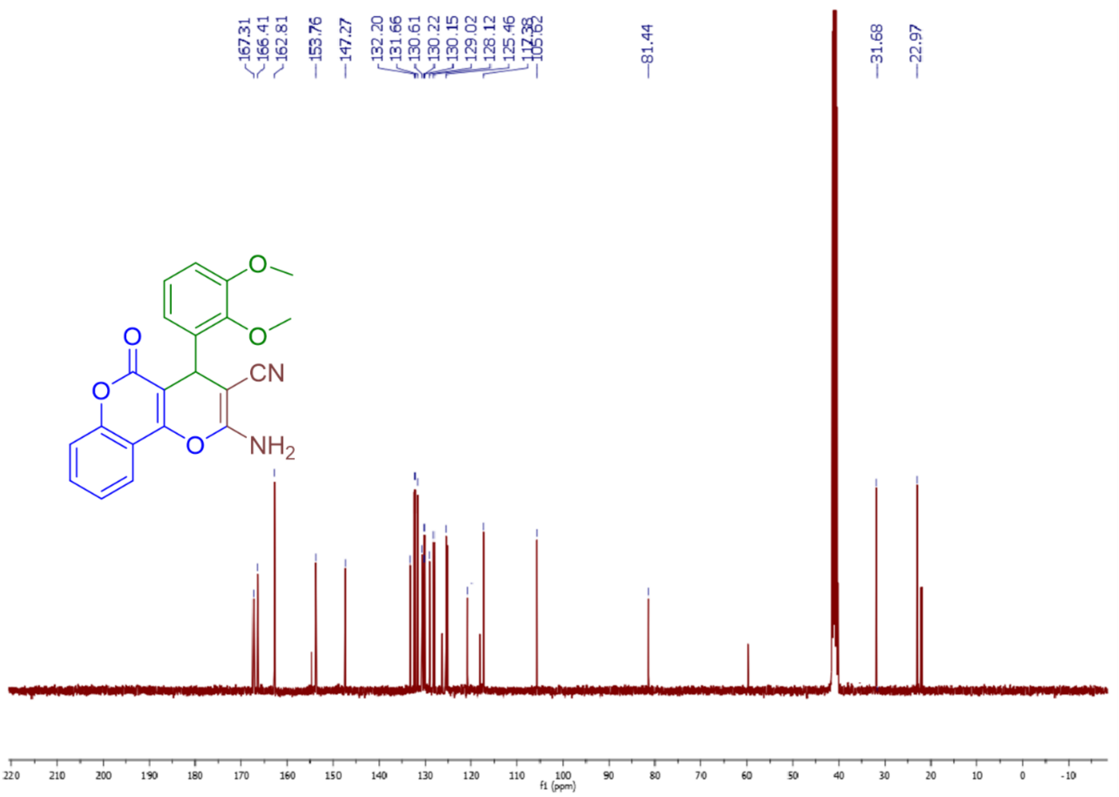

Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum of **5e** in DMSO-*d*$_6$ (100 MHz, 293 K).

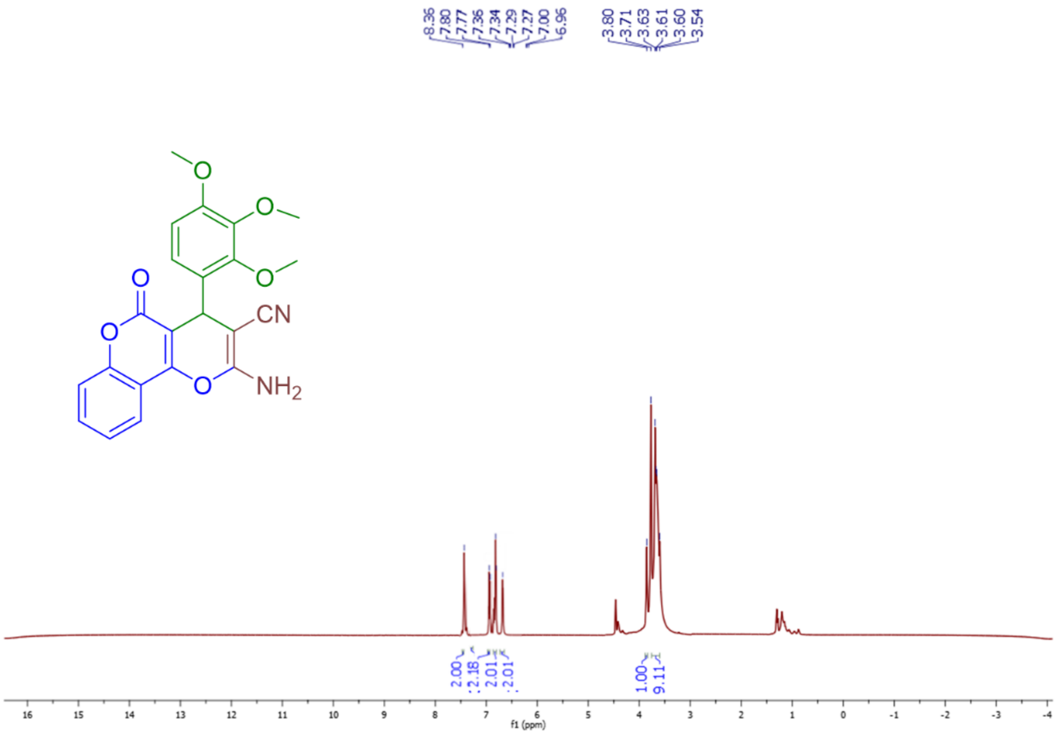

Figure S50. ^{1}H NMR spectrum of **5f** in DMSO-*d*$_6$ (400 MHz, 293 K).

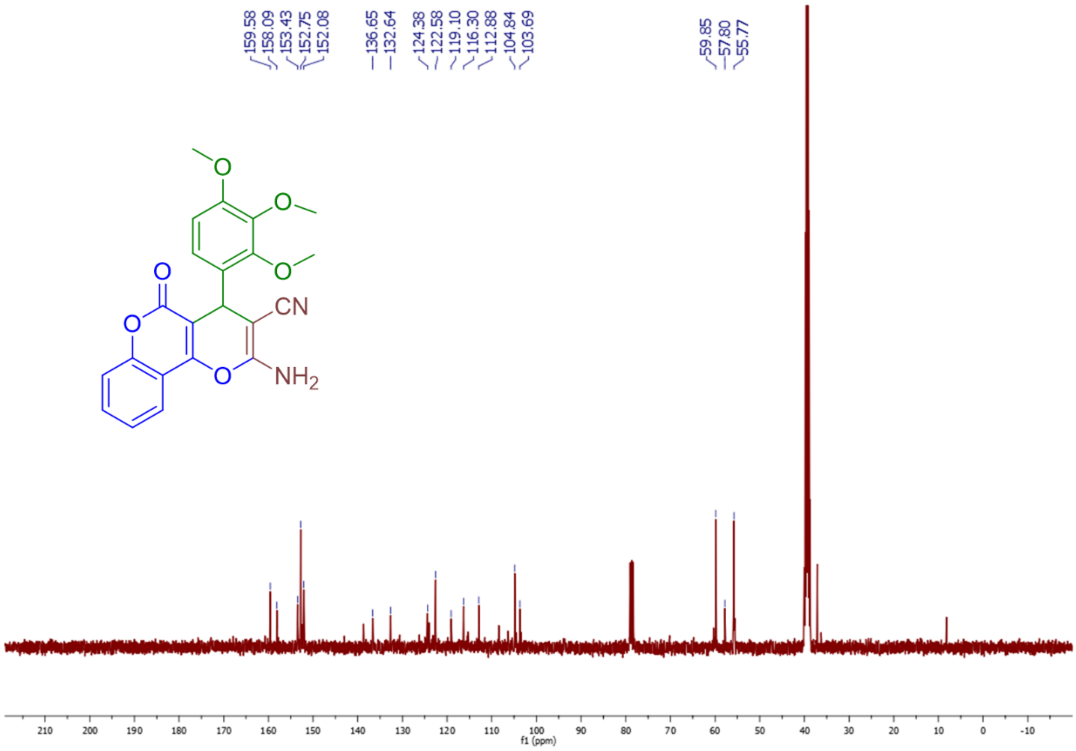

Figure S51. $^{13}C\{^1H\}$ NMR spectrum of **5f** in DMSO-d_6 (100 MHz, 293 K).

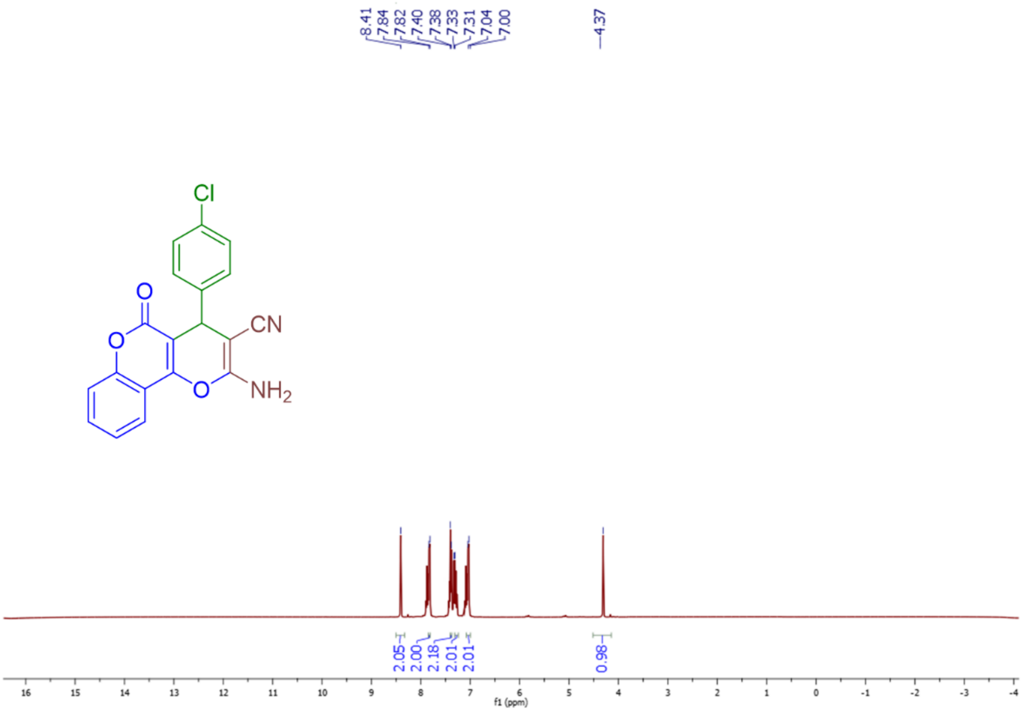

Figure S52. ^1H NMR spectrum **5g** in DMSO-d_6 (400 MHz, 293 K).

Supporting Information

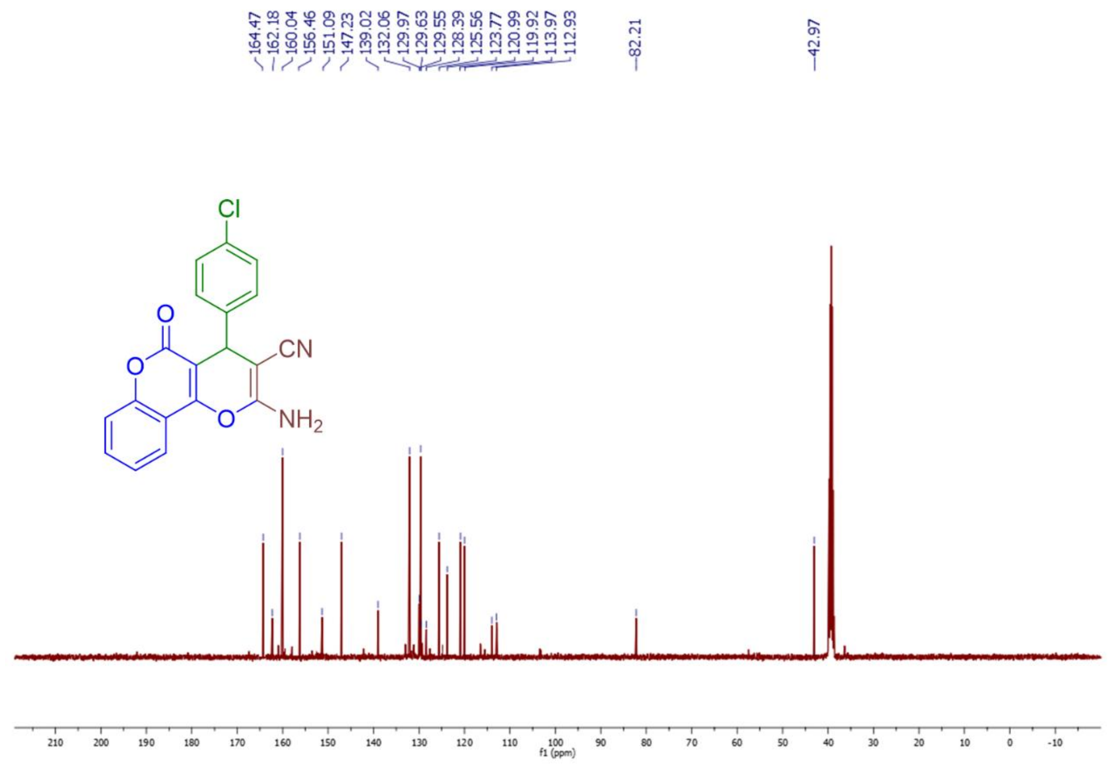

Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum of **5g** in DMSO-d_6 (100 MHz, 293 K).

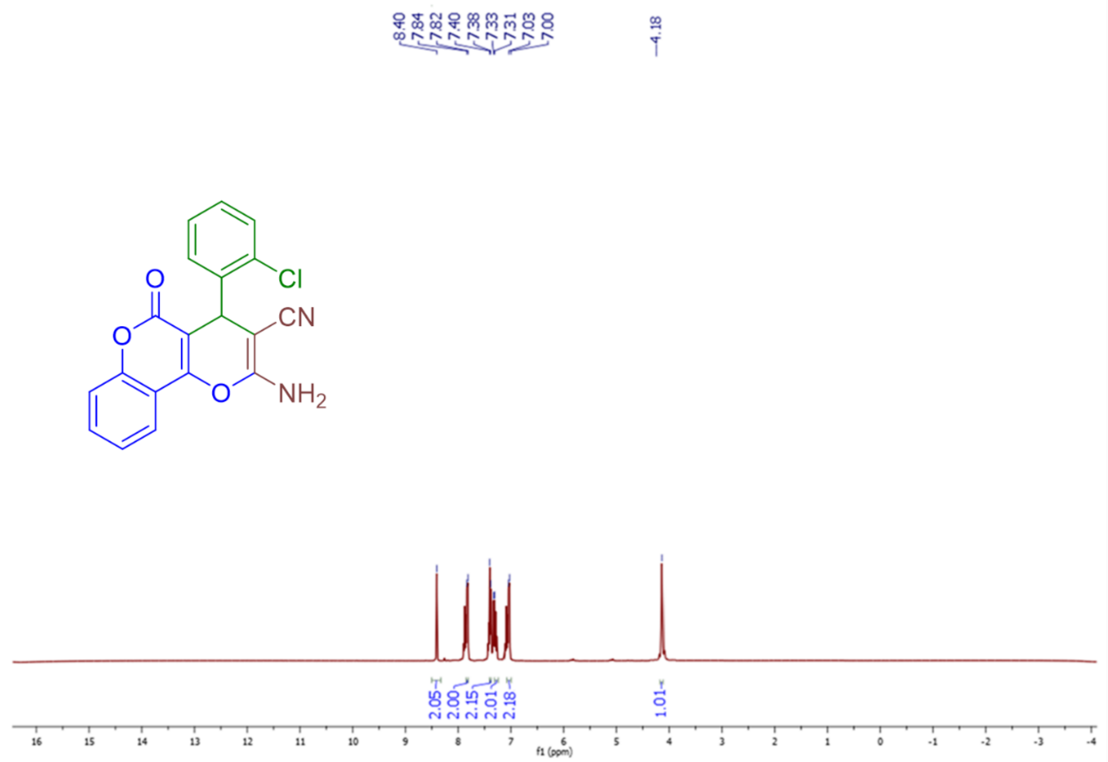

Figure S54. ^{1}H NMR spectrum of **5h** in DMSO-d_6 (400 MHz, 293 K).

Supporting Information

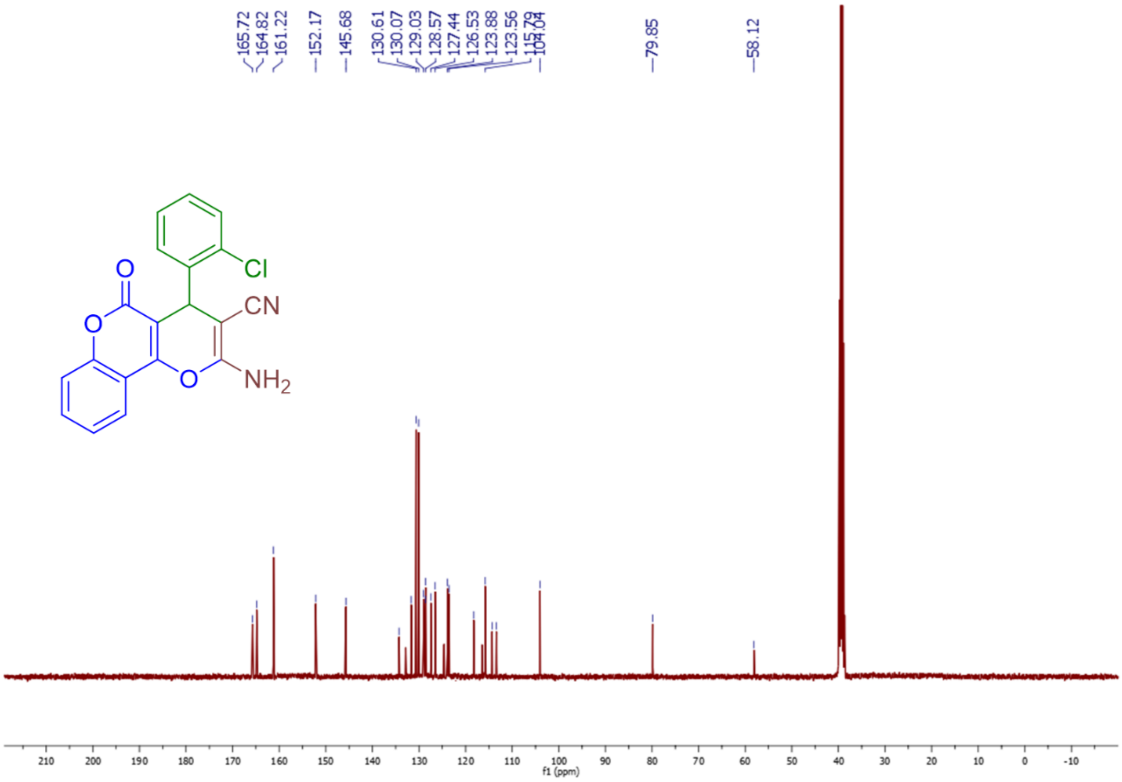

Figure S55. $^{13}C\{^{1}H\}$ NMR spectrum of **5h** in DMSO-d_6 (100 MHz, 293 K).

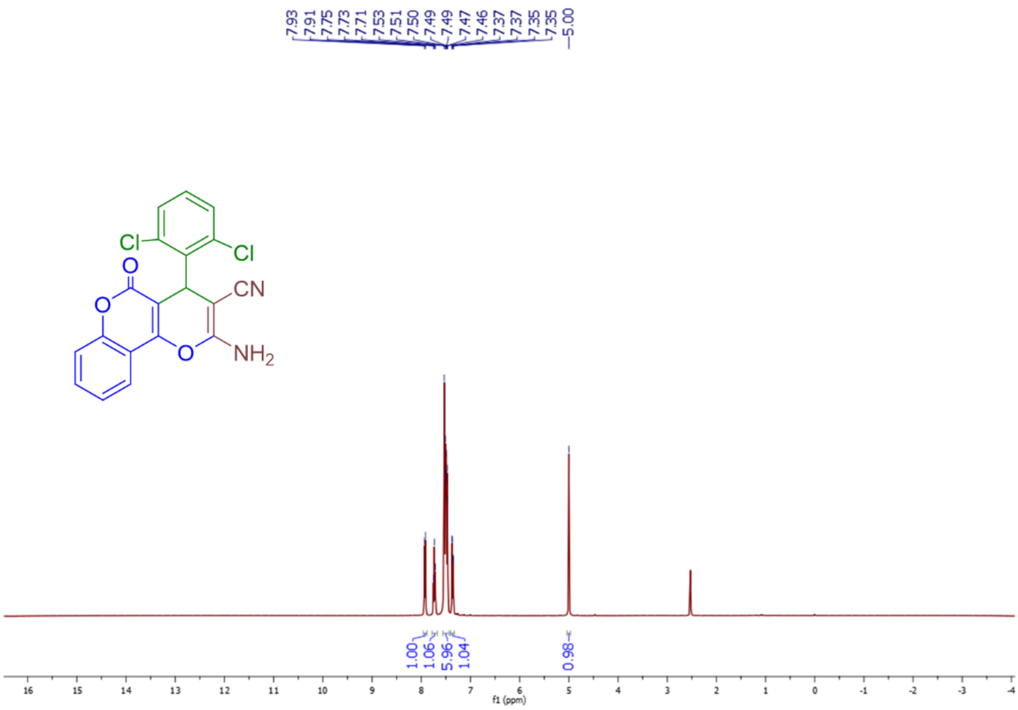

Figure S56. ^{1}H NMR spectrum **5i** in DMSO-d_6 (400 MHz, 293 K).

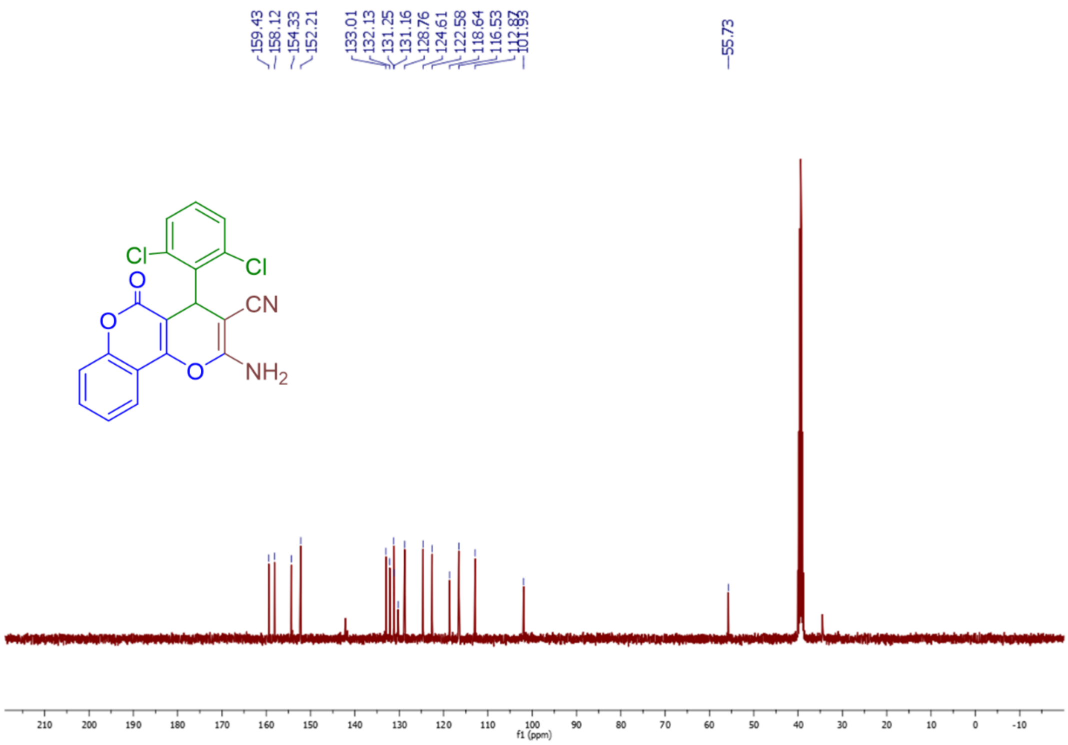

Figure S57. $^{13}C\{^{1}H\}$ NMR spectrum of **5i** in DMSO-d_6 (100 MHz, 293 K).

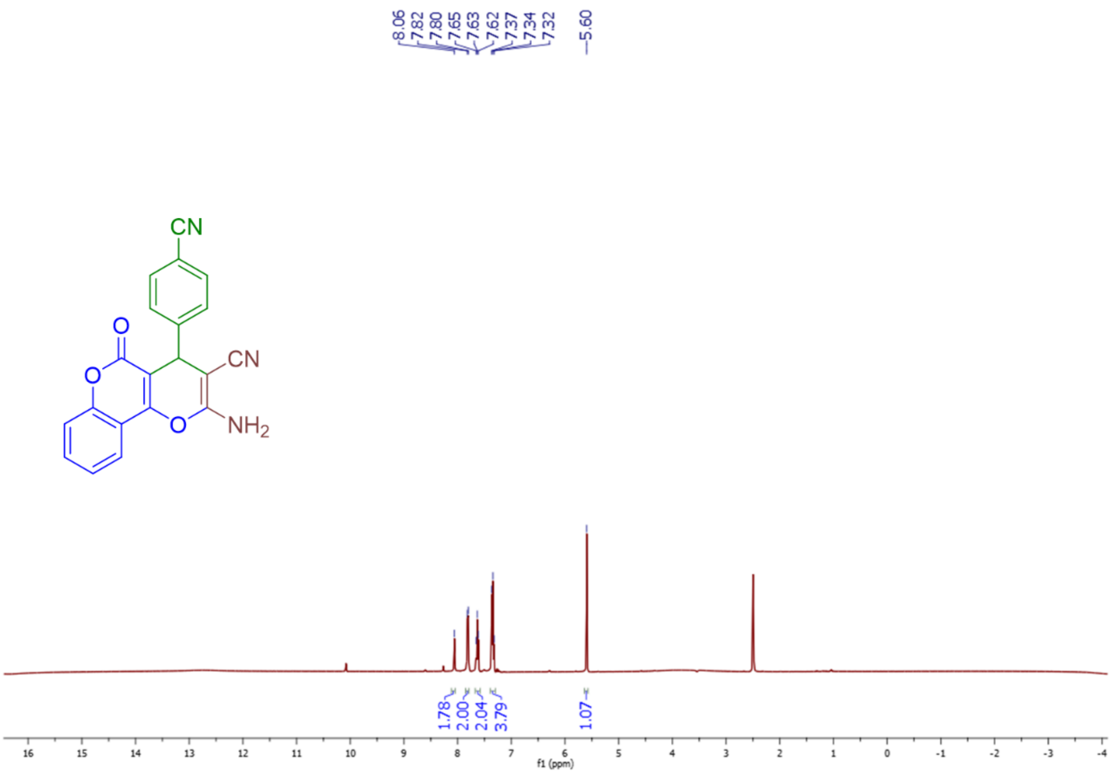

Figure S58. ^{1}H NMR spectrum of **5j** in DMSO-d_6 (400 MHz, 293 K).

Supporting Information

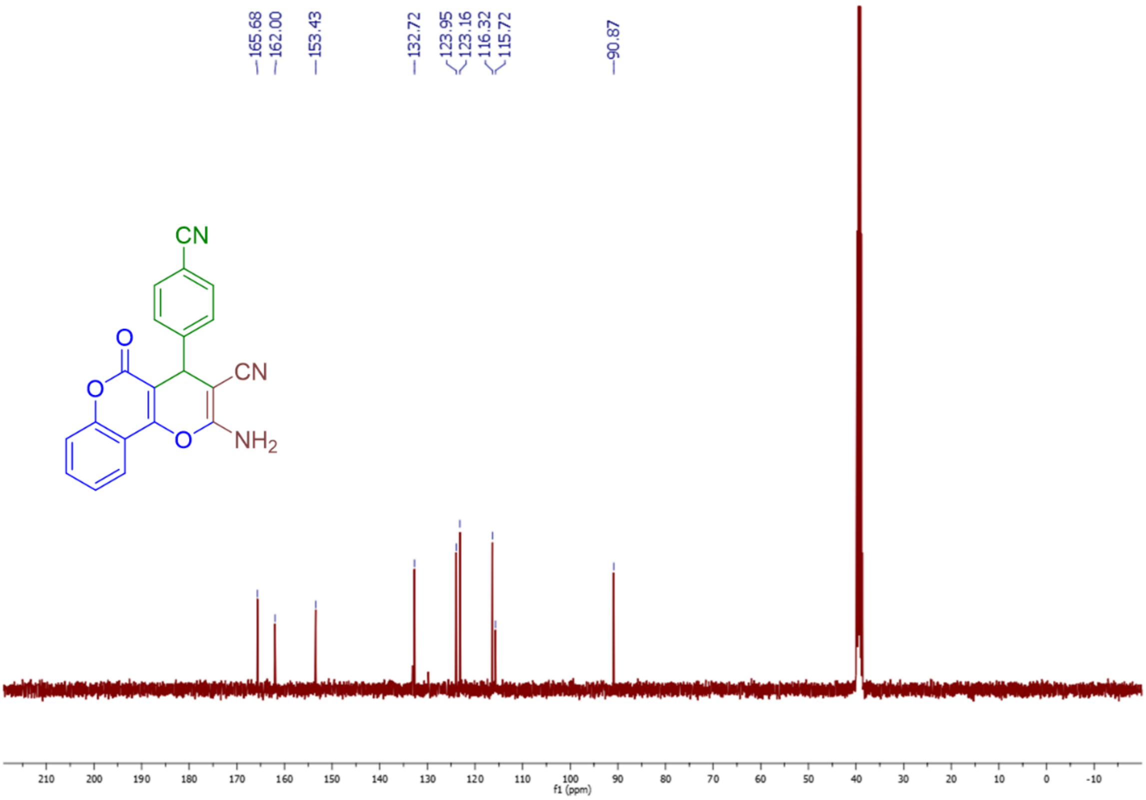

Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum of **5j** in DMSO-d_6 (100 MHz, 293 K).

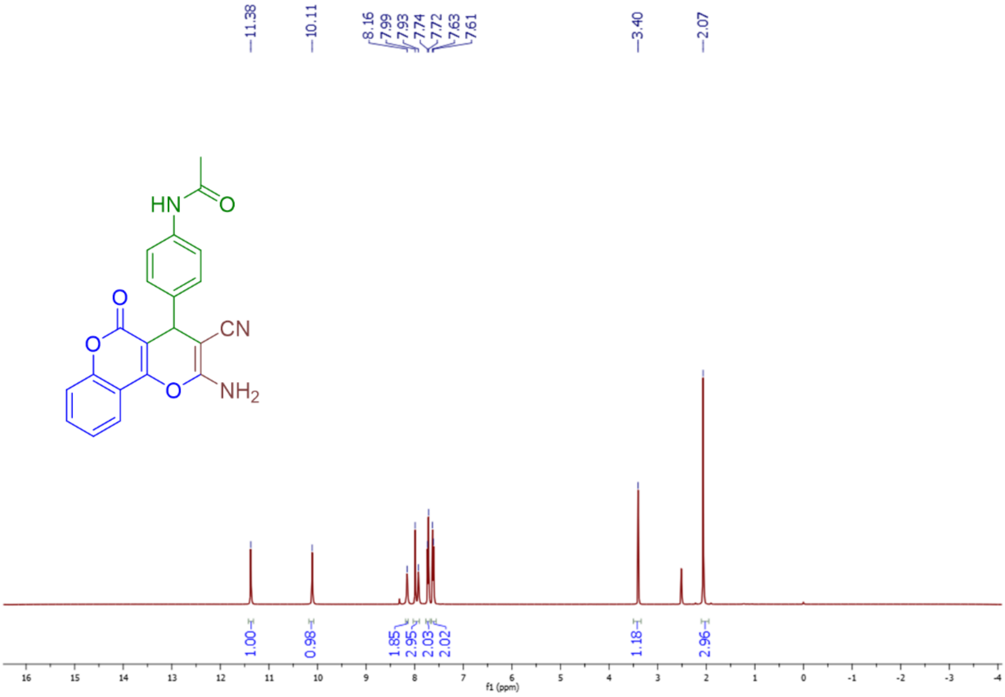

Figure S60. ^{1}H NMR spectrum **5k** in DMSO-d_6 (400 MHz, 293 K).

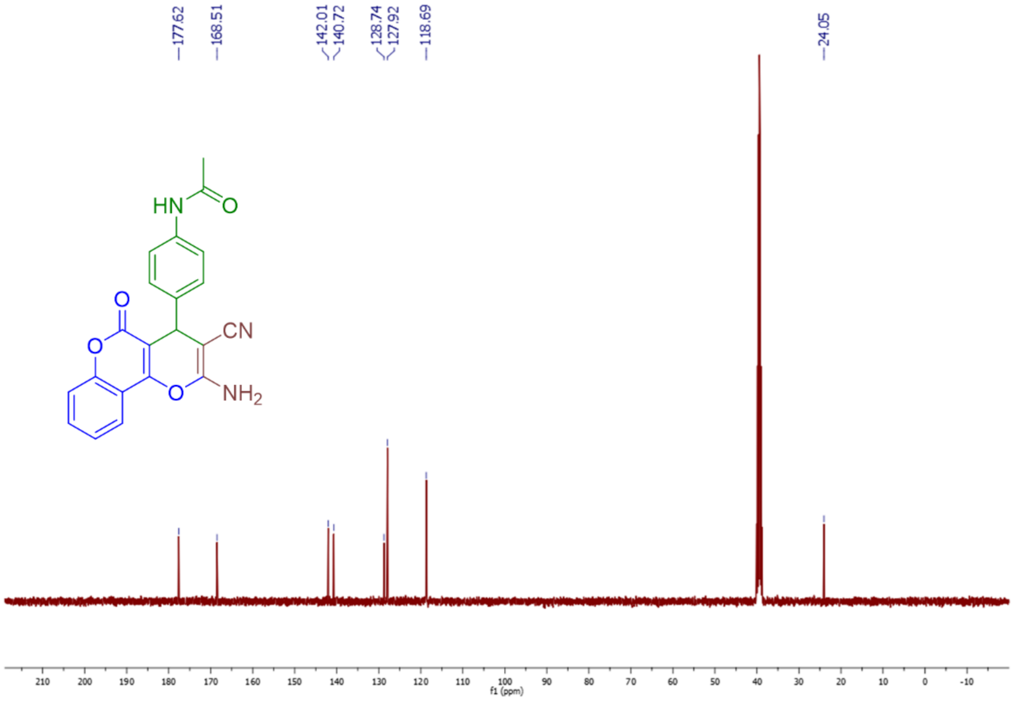

Figure S61. $^{13}C\{^1H\}$ NMR spectrum of **5k** in DMSO-d_6 (100 MHz, 293 K).

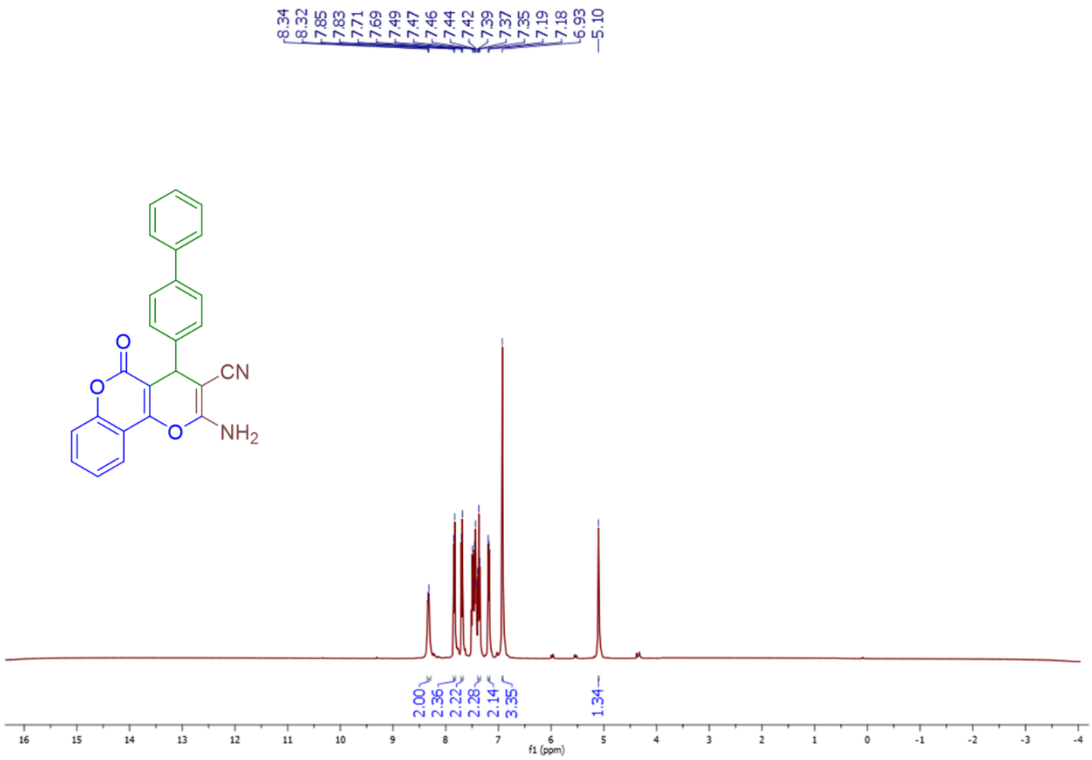

Figure S62. ^1H NMR spectrum of **5l** in DMSO-d_6 (400 MHz, 293 K).

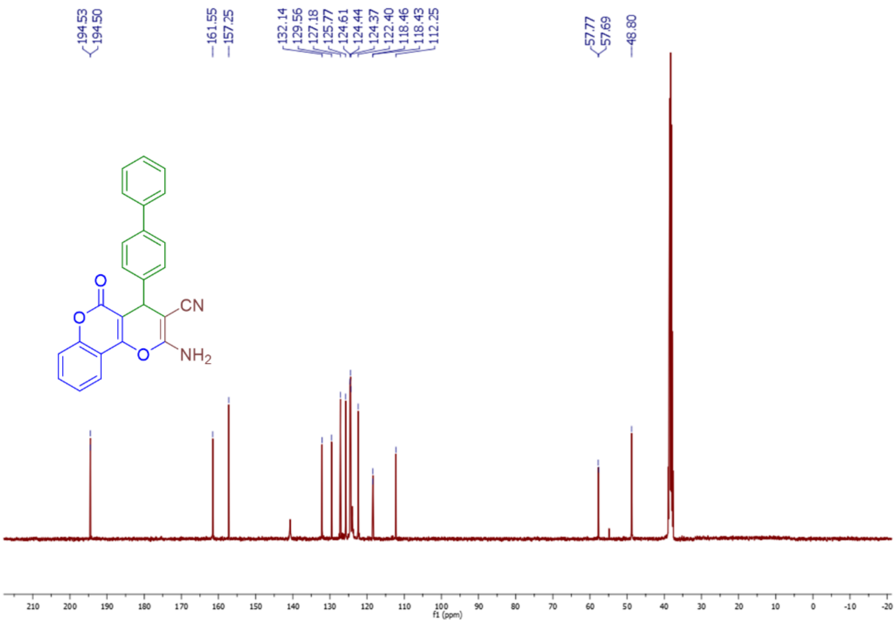

Figure S63. $^{13}C\{^{1}H\}$ NMR spectrum of **5l** in DMSO-d_6 (100 MHz, 293 K).

7. HR-MS of the catalytic products:

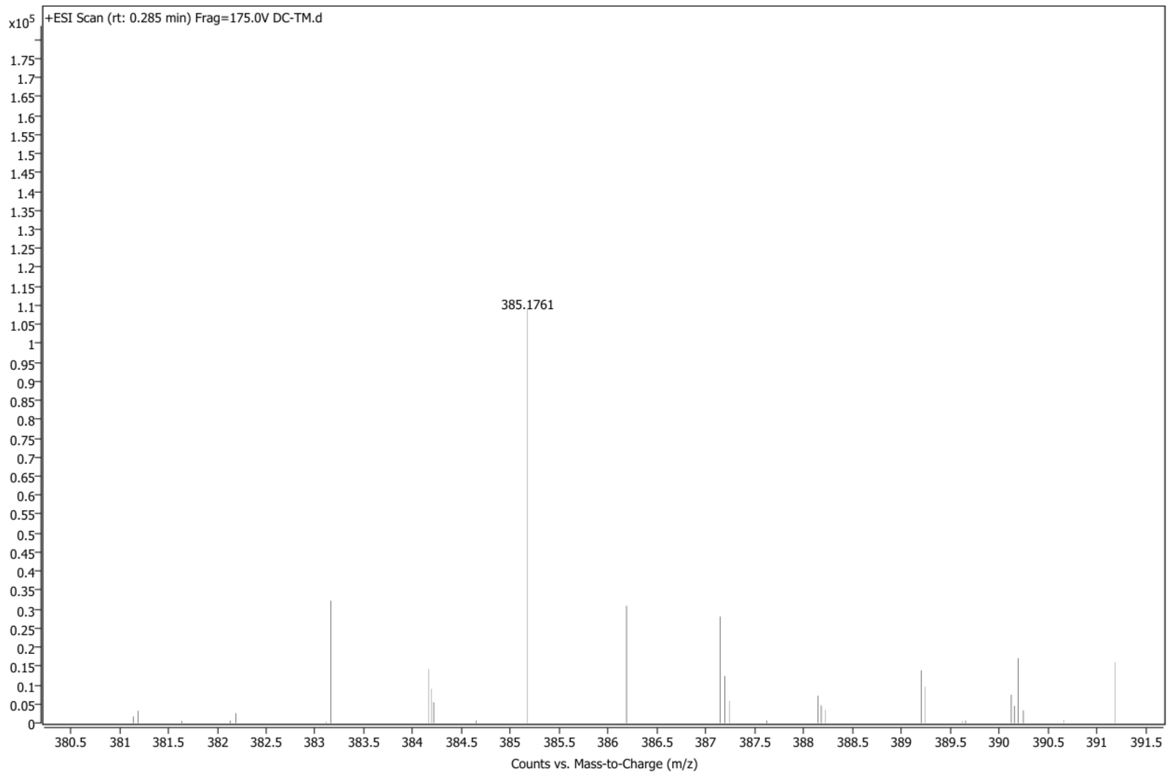

Figure S64. HRMS spectrum of product **4f.**

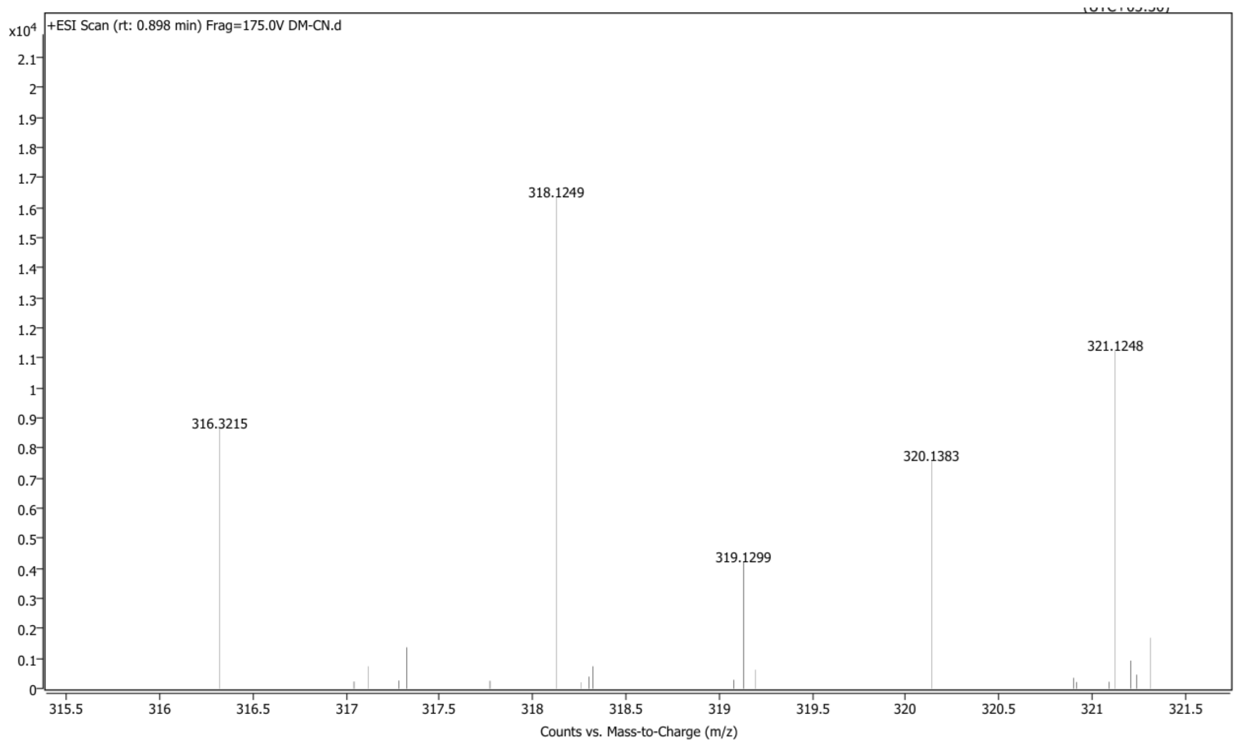

Figure S65. HRMS spectrum of product **4j.**

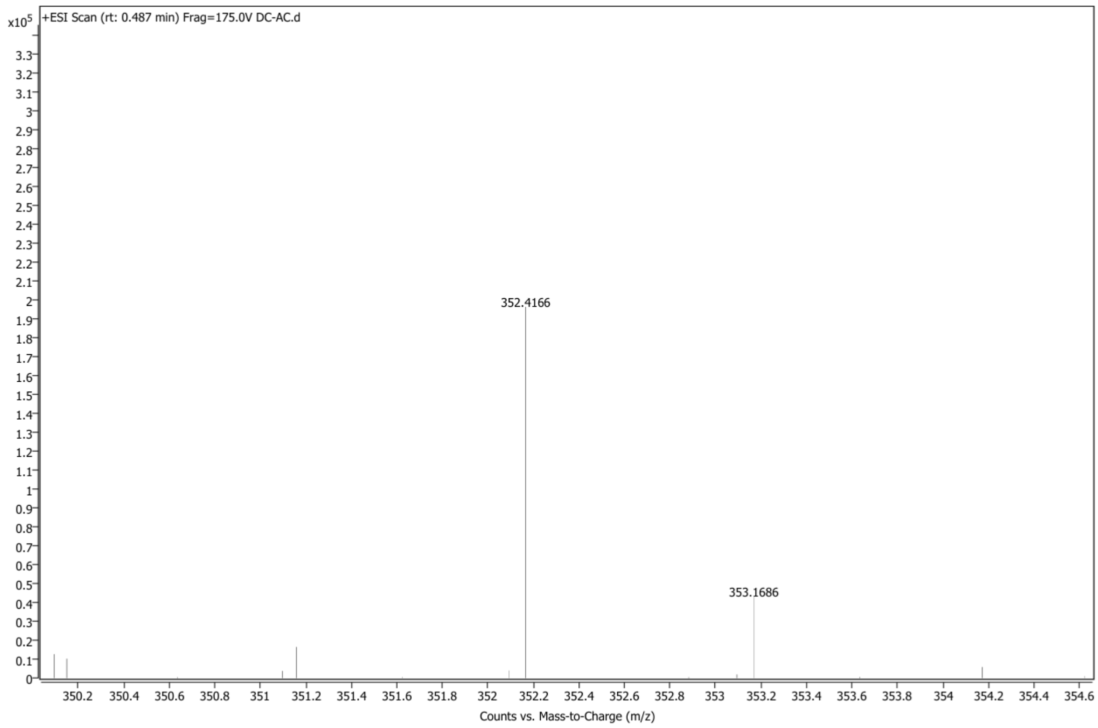

Figure S66. HRMS spectrum of product **4k.**

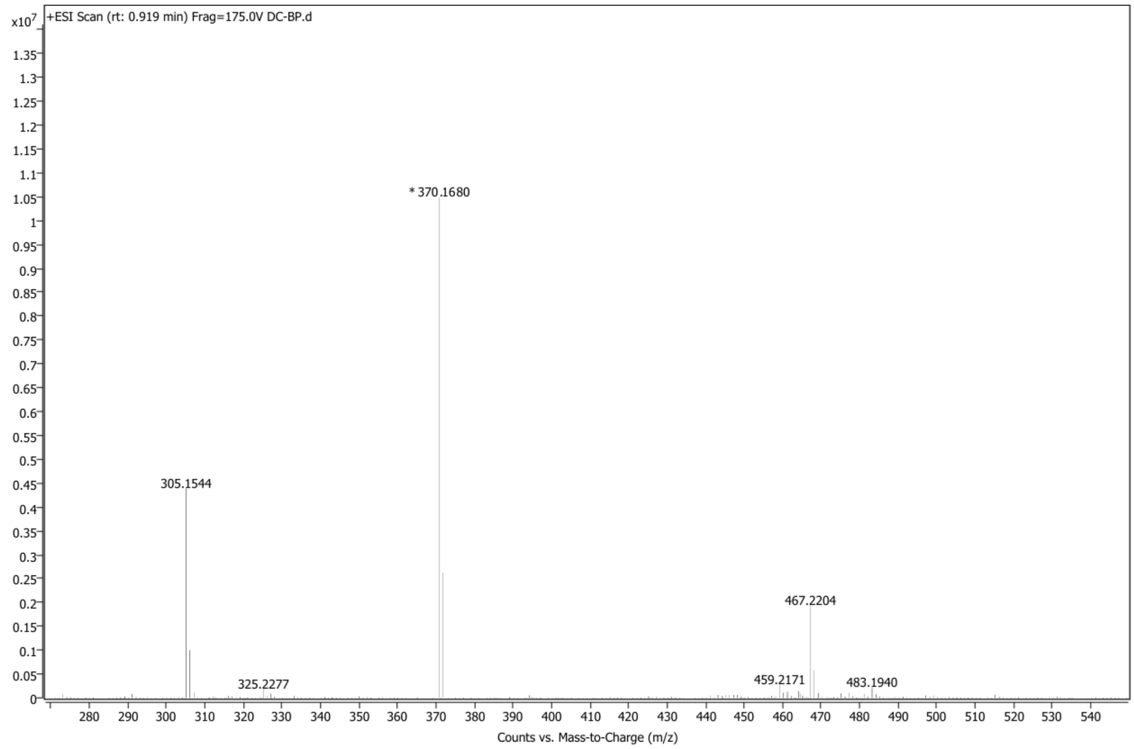

Figure S67. HRMS spectrum of product **4m.**

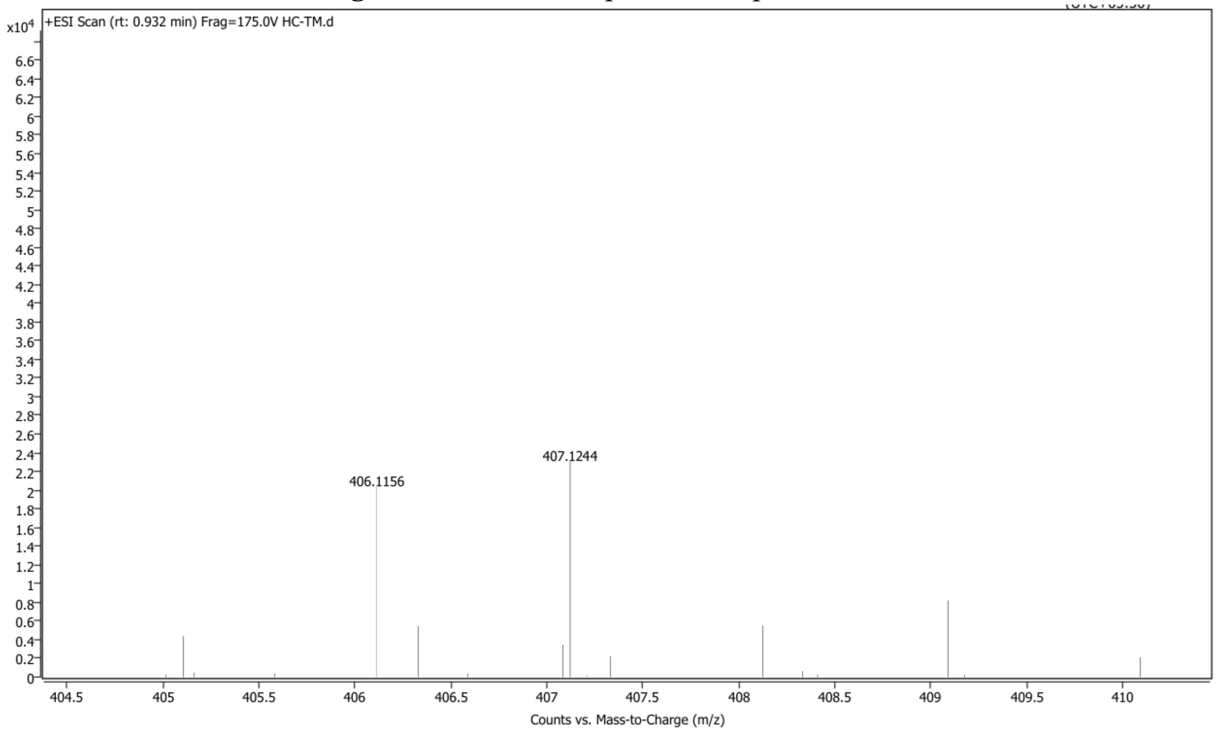

Figure S68. HRMS spectrum of product **5f.**

Supporting Information

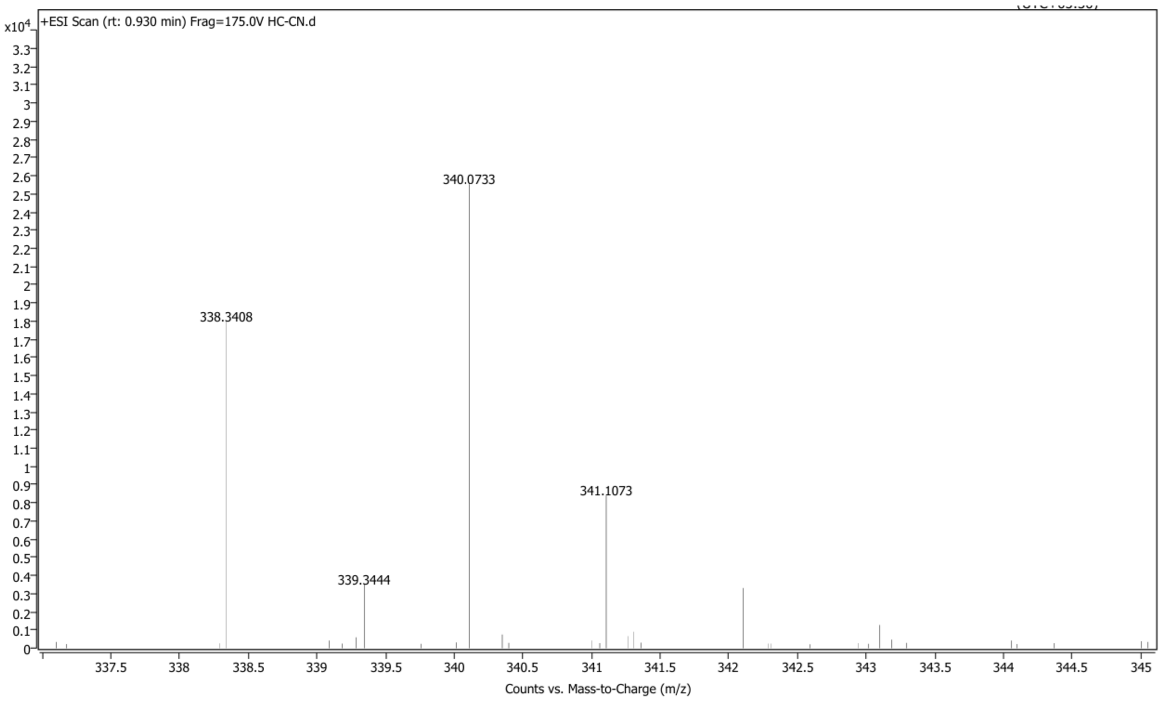

Figure S69. HRMS spectrum of product **5j.**

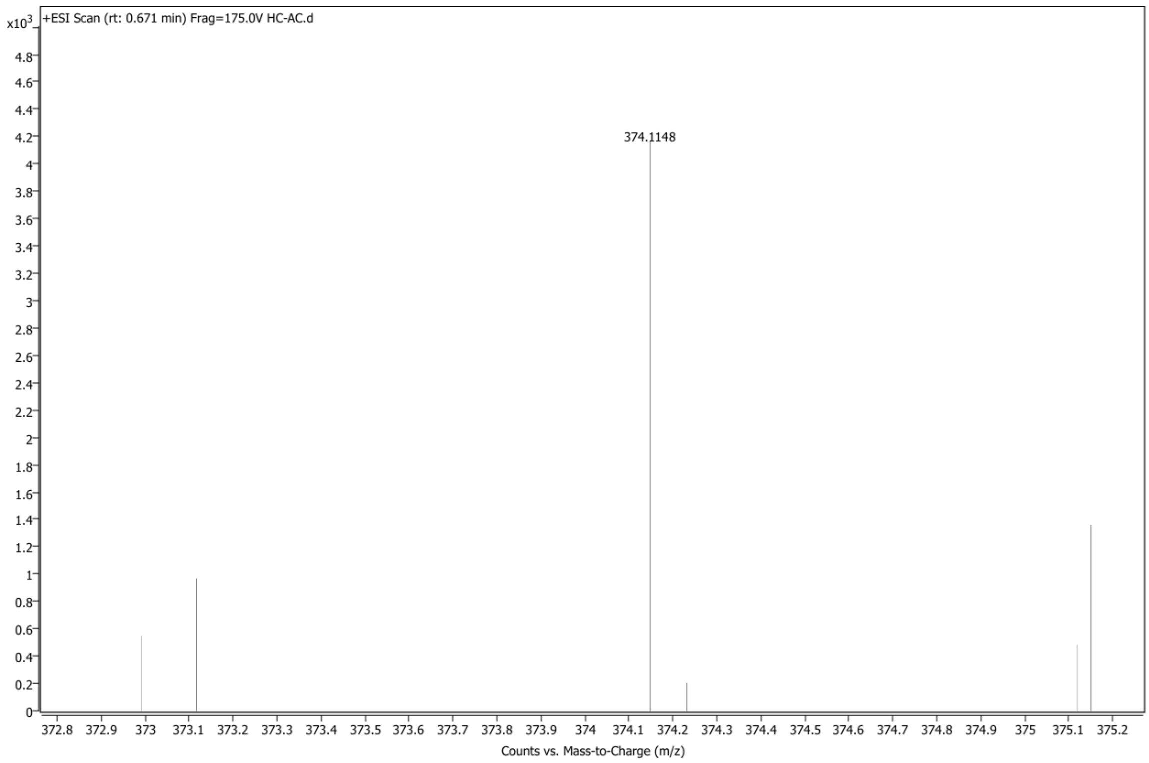

Figure S70. HRMS spectrum of product **5k.**

Supporting Information

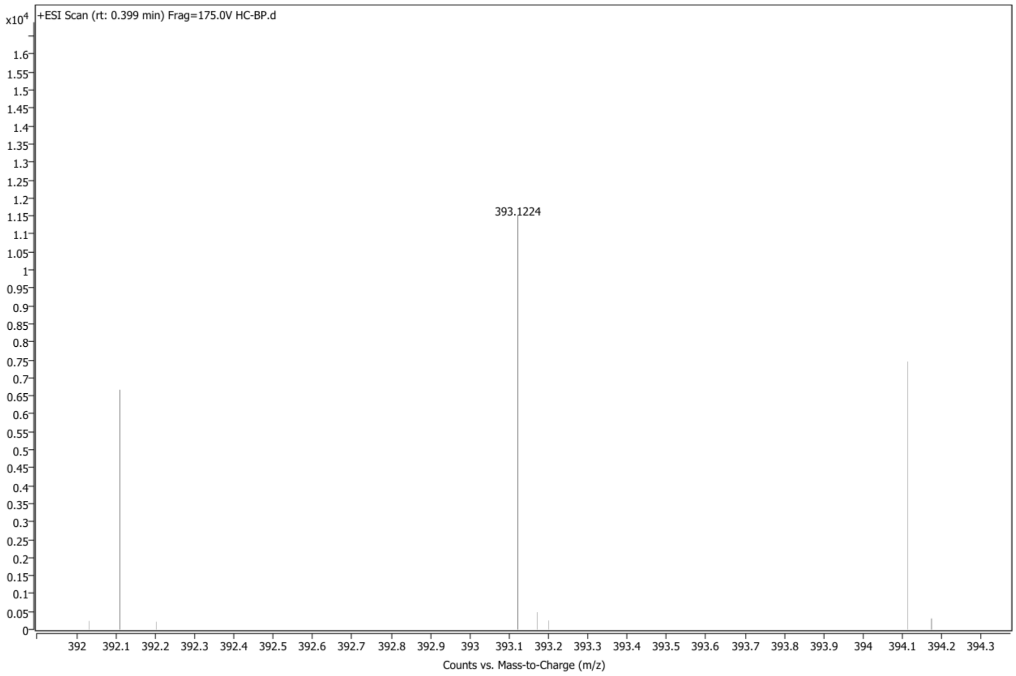

Figure S71. HRMS spectrum of product **5m.**

8. NMR spectra of the intermediates

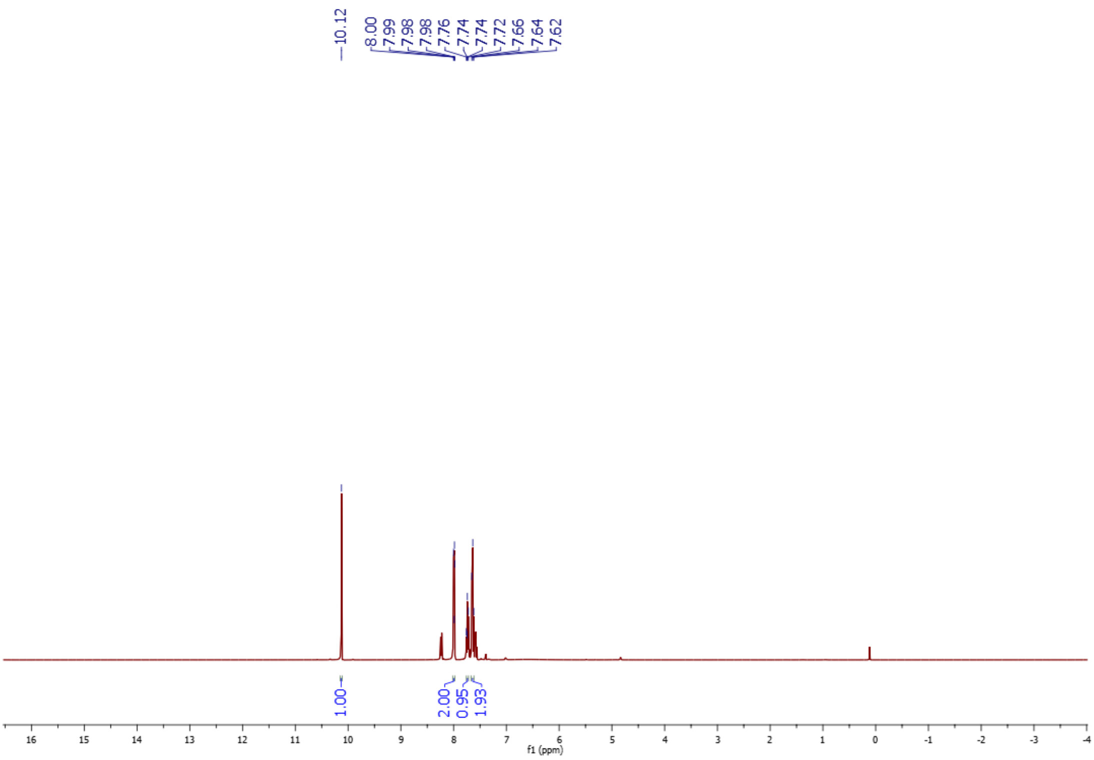

Figure S72. ^{1}H NMR spectrum of intermediate **1a'** in $CDCl_3$ (400 MHz, 293 K).

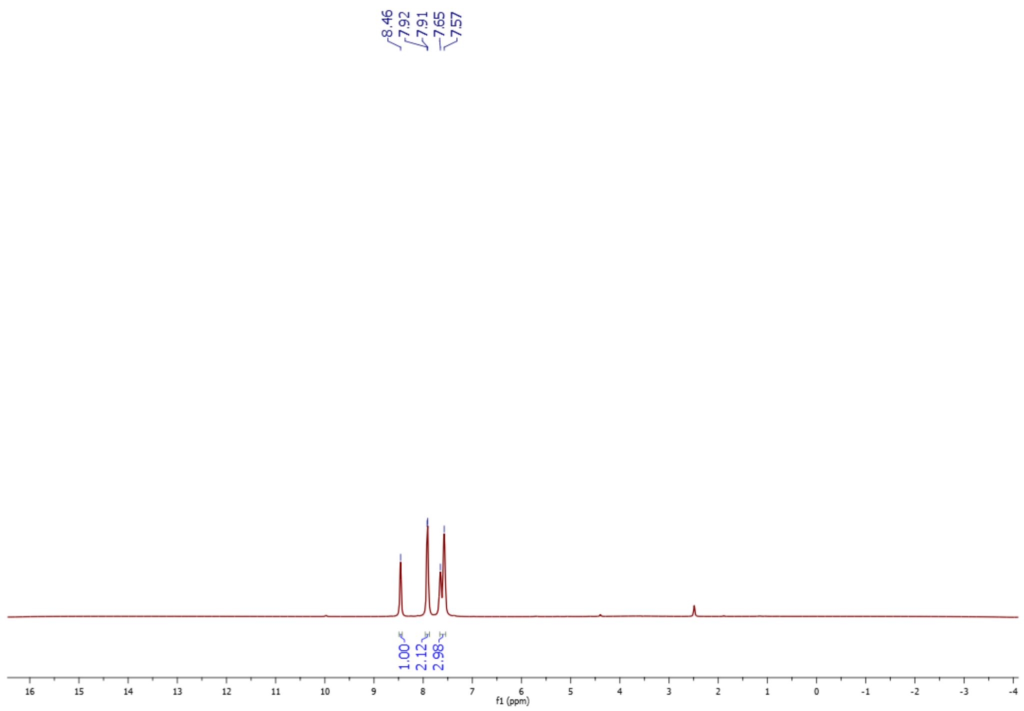

Figure S73. [1]H NMR spectrum of intermediate **2a'** in $CDCl_3$ (400 MHz, 293 K).

9. Confirmation of hydrogen gas

Under N2 atmosphere, a mixture of C2 (2 mol%), t BuOK (2 mmol), benzyl alcohol (1.0 mmol) was dissolved in 3 mL of toluene, the mixture was placed in an oil bath and heated at 110 °C for 5 h. Then, the reaction mixture has been analyzed on GC-TCD detector to witness the liberation of hydrogen gas. (Scheme 5a)

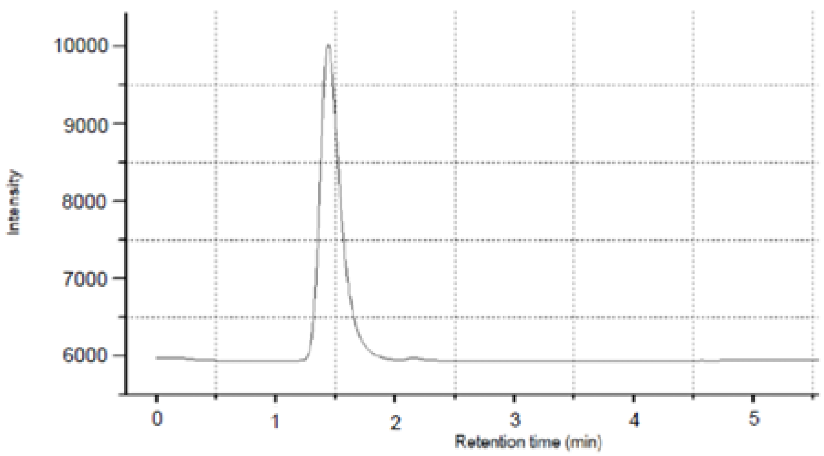

Figure S74. Chromatogram for the evaluation of H_2

10. References:

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