Supplementary Material

o-Nitrophenylacetonitrile Michael additions and cyclocondensations: a novel quinoline synthesis

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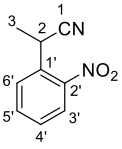
I. SKELETON-NUMBERED STRUCTURES



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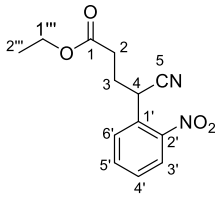

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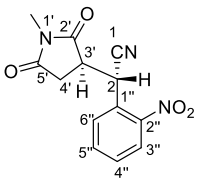

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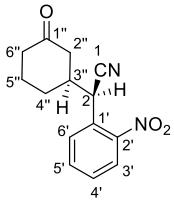

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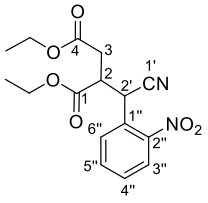

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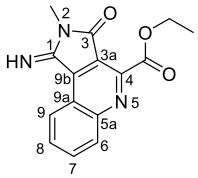

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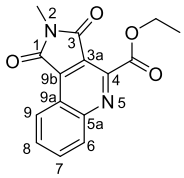

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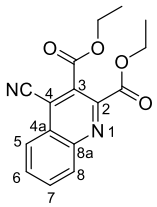

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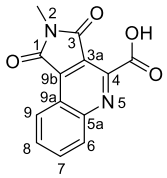

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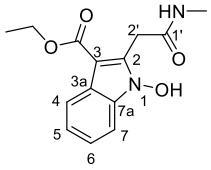

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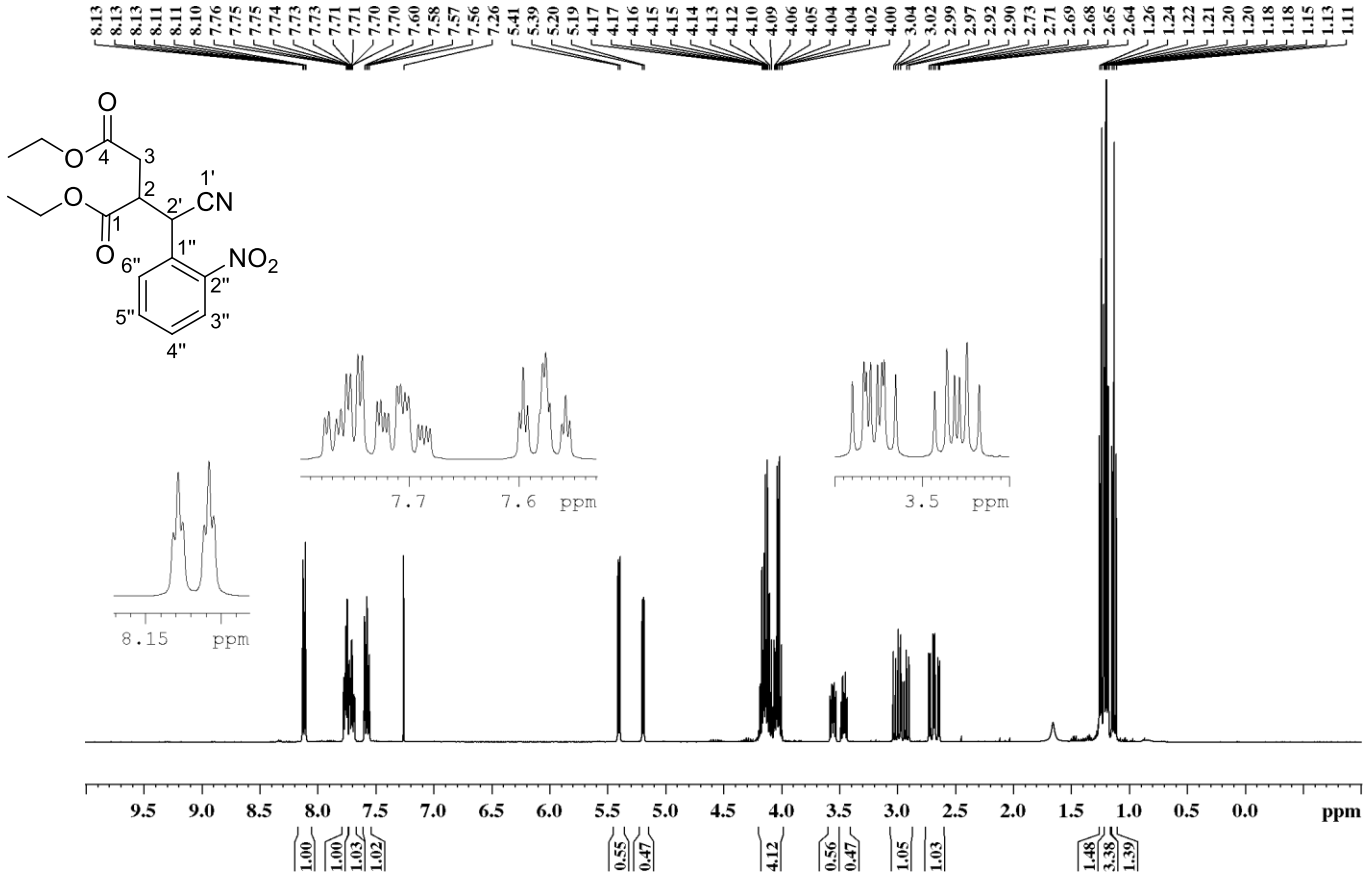
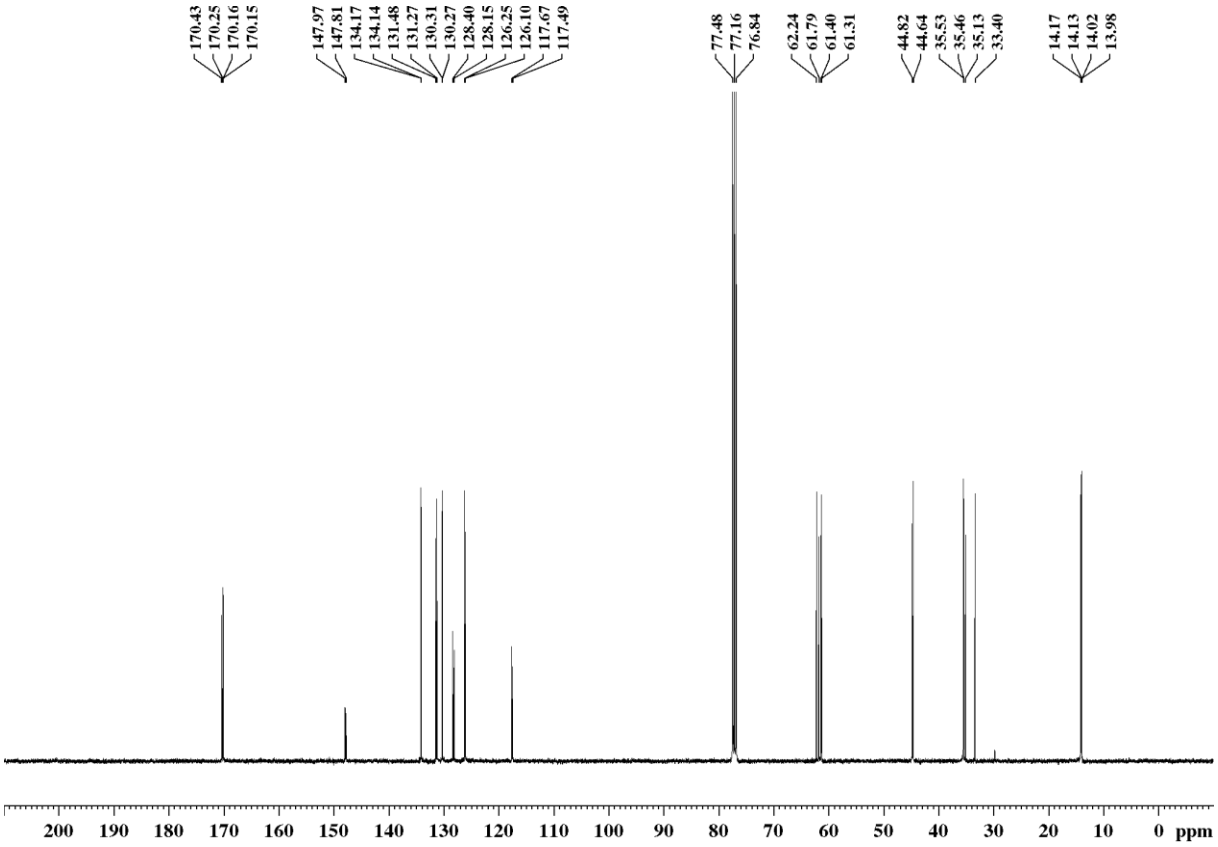
I. NMR SPECTRA

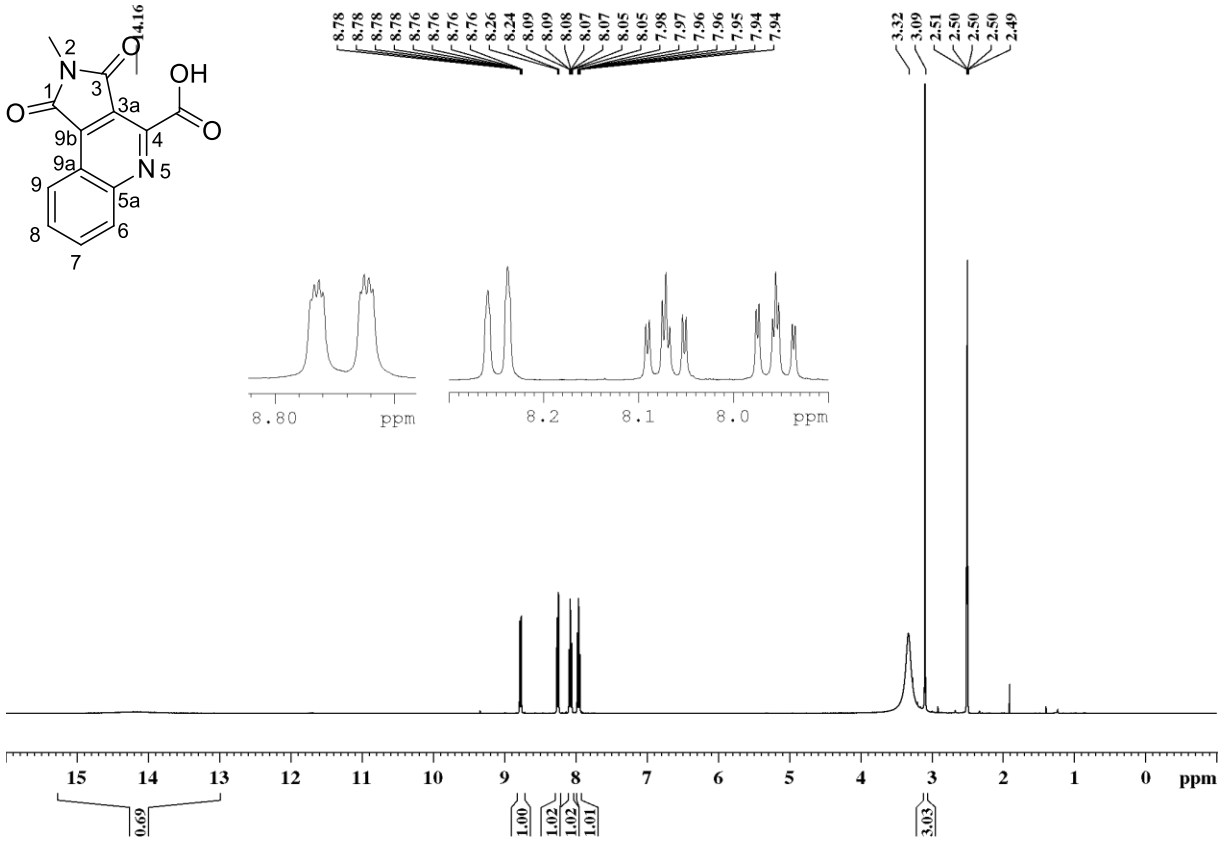
400 MHz ^{1}H NMR spectrum of **17** in $CDCl_3$



100 MHz ^{13}C NMR spectrum of **17** in $CDCl_3$



400 MHz ^{1}H NMR spectrum of **31** in $CDCl_3$



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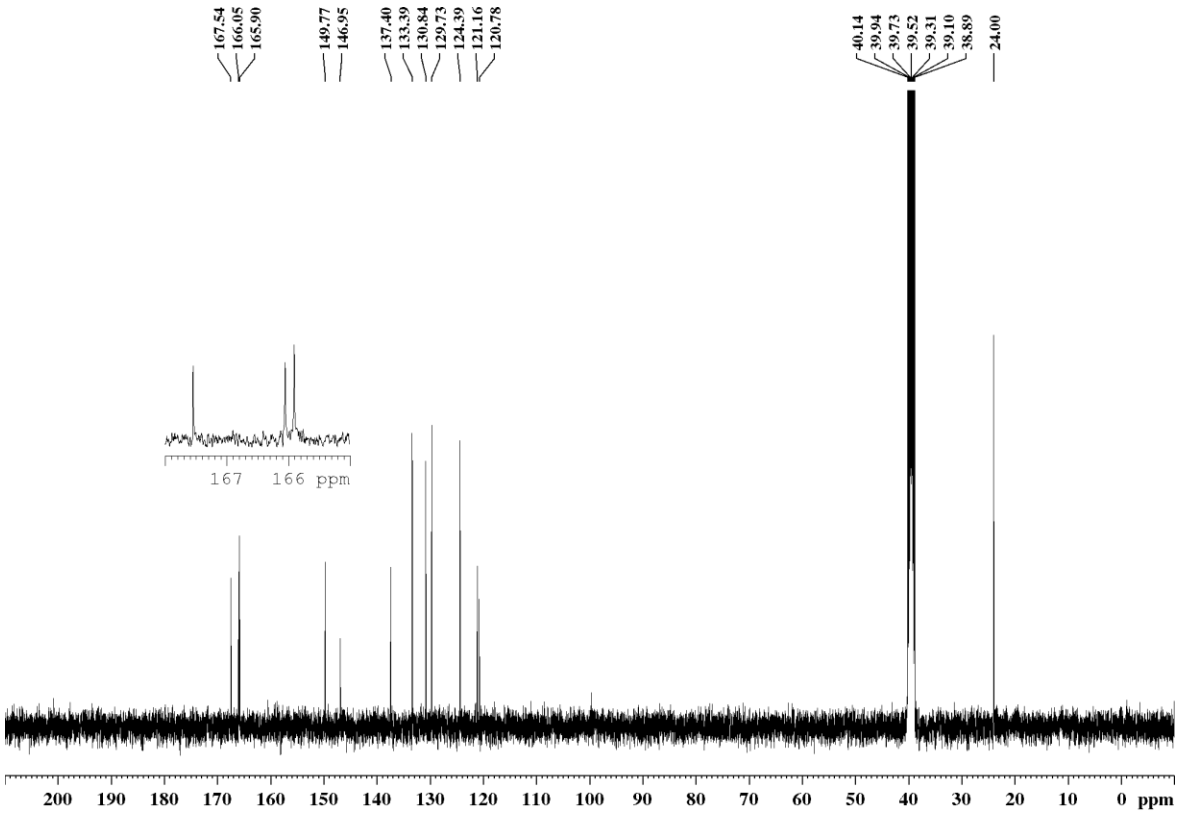
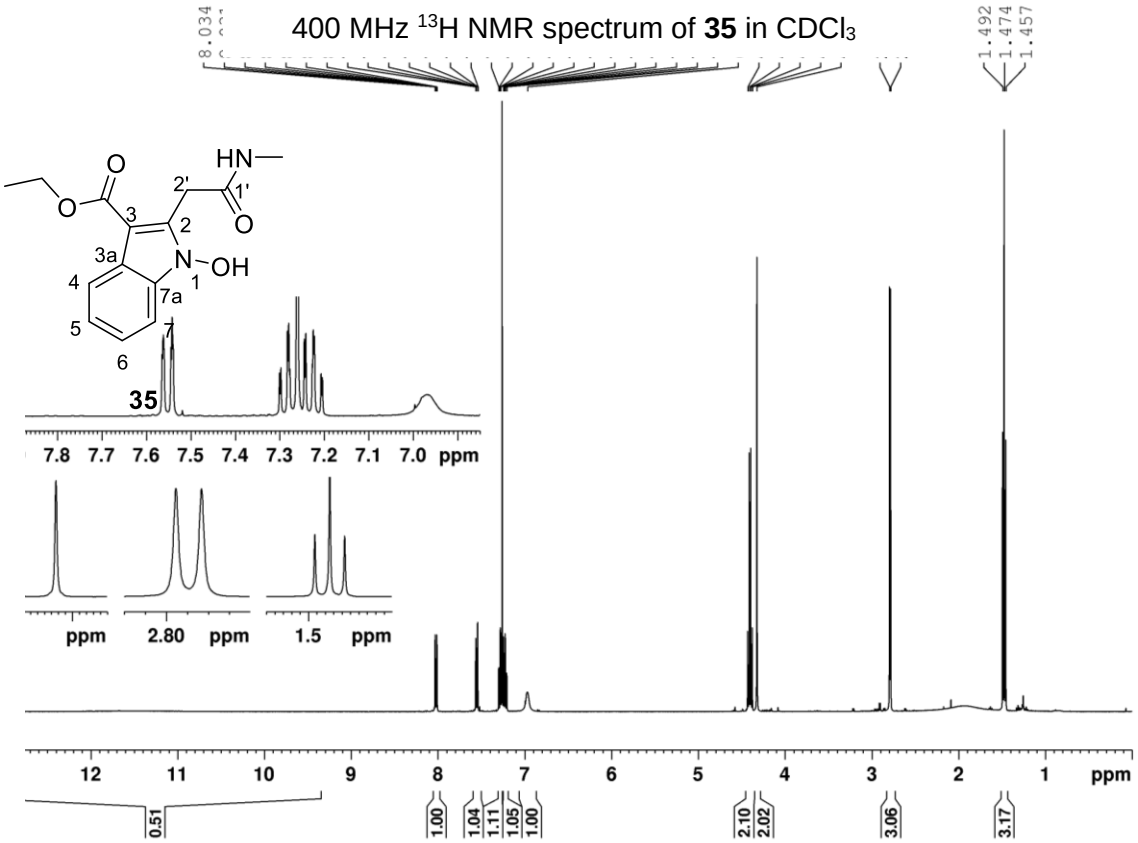
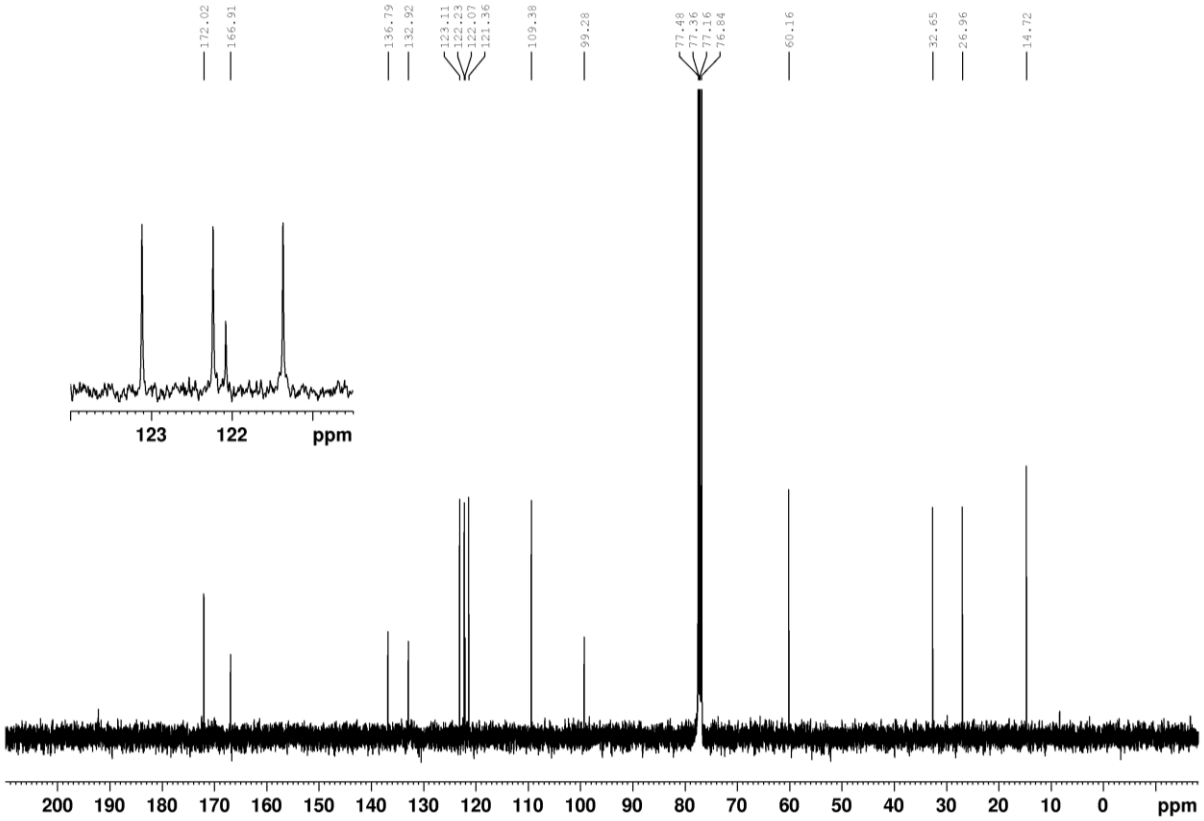


400 MHz ^{13}H NMR spectrum of **35** in $CDCl_3$



100 MHz ^{13}C NMR spectrum of **35** in $CDCl_3$



II. X-RAY CRYSTALLOGRAPHIC DATA

General

Crystallographic data for **15** and **16** were collected at 100(2) K on an Oxford Diffraction Xcalibur diffractometer using Mo Kα radiation (**15**) or an Oxford Diffraction Gemini diffractometer using CuKα radiation (**16**). Following multi-scan absorption corrections and solution by direct methods, the structures were refined against F^2 with full-matrix least-squares using the program SHELXL-2017.[1] All H-atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms. Anisotropic displacement parameters were employed for the non-hydrogen atoms.

Crystallographic data for **21** and **22** were collected at 110 K on a Rigaku Saturn 70 CCD diffractometer with graphite monochromated Mo Kα radiation. Data were collected and processed using Crysal-Clear (Rigaku) software. The structures were solved with the ShelXT 2018/2[2] solution program using dual methods and by using Olex2 1.5[3] as the graphical interface. The model was refined with XL[1] using full matrix least squares minimisation on F^2. All H-atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms. Anisotropic displacement parameters were employed for the non-hydrogen atoms.

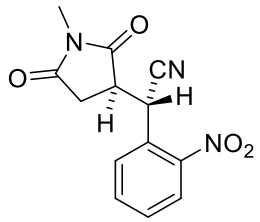
Crystallographic data for **31** were collected on a XtaLAB Synergy, Single source HyPix diffractometer. The crystal was kept at a steady T = 100.00(10) K during data collection. The structure was solved with the ShelXT 2018/2[2] solution program using dual methods and by using Olex2 1.5[3] as the graphical interface. The model was refined with XL[1] using full matrix least squares minimisation on F^2. Anisotropic displacement parameters were employed for the non-hydrogen atoms.

Crystallographic data for **39** were collected at 200(2) K, (rather than 100 K as there were indications that the crystal deteriorated at lower temperatures) on an Oxford Diffraction Gemini diffractometer using Cu Kα radiation. Other details are as for **15** and **16**.

References

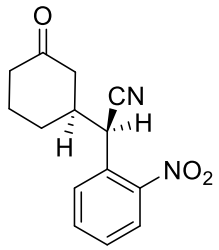
1. Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3-8.
2. Sheldrick, G. M., SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3-8.
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339-341.

Table S1. Crystallographic data for (S*)-2-((R*)-1'-methyl-2',5'-dioxopyrrolidin-3'-yl)-2-(2''-nitrophenyl)acetonitrile (**15**)



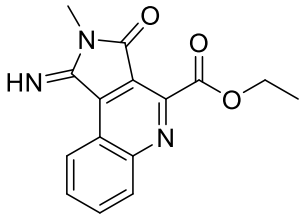
Empirical formula	$C_{13}H_{11}N_3O_4$
Formula weight	273.25
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 9.9636(6) Å
	b = 16.3916(9) Å
	c = 7.4181(4) Å
	β= 90.580(5)°
Volume	1211.46(12) Å^3
Z	4
Density (calculated)	1.498 Mg/m^3
Absorption coefficient	0.114 mm^{-1}
F(000)	568
Crystal size	0.40 × 0.21 × 0.05 mm^3
θ range for data collection	3.01 to 32.21°.
Index ranges	–13<=h<=14, –23<=k<=23, –10<=l<=11
Reflections collected	13906
Independent reflections	4005 [R(int) = 0.0413]
Completeness to θ = 31.00°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max./min. transmission	1.00/0.97
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4005 / 0 / 182
Goodness-of-fit on F^2	0.893
Final R indices [I>2σ(I)]	R_1 = 0.0438, wR_2 = 0.0992
R indices (all data)	R_1 = 0.0764, wR_2 = 0.1061
Largest diff. peak and hole	0.402 and –0.342 e.Å^{-3}
CCDC	1829603

Table S2. Crystallographic data for (S*)-2-(2'-nitrophenyl)-2-((S*)-3''-oxocyclohexyl)acetonitrile (**16**)



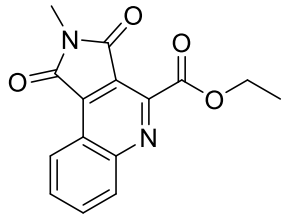
Empirical formula	$C_{14}H_{14}N_2O_3$
Formula weight	258.27
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 21.7836(5) Å
	b = 14.3008(3) Å
	c = 7.9630(2) Å
	β= 95.663(2)°
Volume	2468.55(10) Å^3
Z	8
Density (calculated)	1.390 Mg/m^3
Absorption coefficient	0.819 mm^{-1}
F(000)	1088
Crystal size	0.27 × 0.05 × 0.05 mm^3
θ range for data collection	3.70 to 67.24°.
Index ranges	–26<=h<=19, –17<=k<=16, –9<=l<=9
Reflections collected	23554
Independent reflections	4409 [R(int) = 0.0375]
Completeness to θ = 67.24°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max./min. transmission	1.00/0.91
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4409 / 0 / 343
Goodness-of-fit on F^2	1.040
Final R indices [I>2σ(I)]	R_1 = 0.0427, wR_2 = 0.1134
R indices (all data)	R_1 = 0.0527, wR_2 = 0.1205
Largest diff. peak and hole	0.459 and –0.179 e.Å^{-3}
CCDC	1829658

Table S3. Crystallographic data for ethyl 1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinoline-4-carboxylate (**21**)



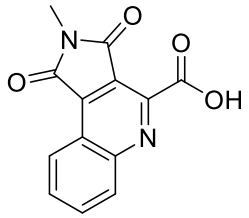
Empirical formula	$C_{15}H_{13}N_3O_3$
Formula weight	283.28
Temperature	110 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 7.873(4) Å
	b = 18.882(8) Å
	c = 8.723(4) Å
	β= 97.066(6)°
Volume	1286.78(1) Å^3
Z	4
Density (calculated)	1.462 Mg/m^3
Absorption coefficient	0.105 mm^{-1}
F(000)	592
Crystal size	0.33 × 0.18 × 0.11 mm^3
θ range for data collection	2.59 to 24.50°
Index ranges	–9<=h<=6, –14<=k<=22, –10<=l<=10
Reflections collected	7299
Independent reflections	2097 [R(int) = 0.062]
Completeness to θ = 24.50°	98.0 %
Absorption correction	Multi-scan from equivalents
Max./min. transmission	0.99/0.97
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2097 / 0 / 194
Goodness-of-fit on F^2	1.236
Final R indices [I>2σ(I)]	R_1 = 0.0945, wR_2 = 0.2353
R indices (all data)	R_1 = 0.1143, wR_2 = 0.2533
Largest diff. peak and hole	0.393 and –0.306 e.Å^{-3}
CCDC	2182720

Table S4. Crystallographic data for ethyl 2-methyl-1,3-dioxo-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinoline-4-carboxylate (**22**)



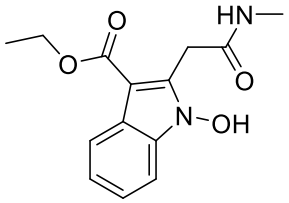
Identification code	SYJ-80
Empirical formula	$C_{15}H_{12}N_2O_4$
Formula weight	284.27
Temperature	110 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.213(7) Å
	b = 4.615(3) Å
	c = 24.59(1) Å
	β= 95.438(7)°
Volume	1266.59(1) Å^3
Z	4
Density (calculated)	1.491 Mg/m^3
Absorption coefficient	1.101 mm^{-1}
F(000)	592
Crystal size	0.33 × 0.13 × 0.11 mm^3
θ range for data collection	1.66 to 24.49°.
Index ranges	–13<=h<=12, –4<=k<=5, –22<=l<=28
Reflections collected	7556
Independent reflections	2096 [R(int) = 0.0475]
Completeness to θ = 67.24°	99.2 %
Absorption correction	Multi-scan from equivalents
Max./min. transmission	0.99/0.96
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2096 / 0 / 190
Goodness-of-fit on F^2	1.242
Final R indices [I>2σ(I)]	R_1 = 0.0913, wR_2 = 0.2413
R indices (all data)	R_1 = 0.0969, wR_2 = 0.2491
Largest diff. peak and hole	0.556 and –0.446 e.Å^{-3}
CCDC	2182719

Table S5. Crystallographic data for 2-methyl-1,3-dioxo-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinoline-4-carboxylic acid (**31**)



Empirical formula	$C_{13}H_8N_2O_4$
Formula weight	256.21
Temperature	100(10) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 9.16540(10) Å
	b = 10.29660(10) Å
	c = 11.57210(10) Å
	β= 100.4360(10)°
Volume	1074.022(19) Å^3
Z	4
Density (calculated)	1.585 Mg/m^3
Absorption coefficient	1.019 mm^{-1}
F(000)	528
Crystal size	0.11 × 0.08 × 0.03 mm^3
θ range for data collection	5.68 to 75.46°.
Index ranges	–11<=h<=11, –12<=k<=12, –14<=l<=14
Reflections collected	38176
Independent reflections	2195 [R(int) = 0.0477]
Completeness to θ = 150.9°	98 %
Absorption correction	Semi-empirical from equivalents
Max./min. transmission	0.811/1.00
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2195 / 0 / 174
Goodness-of-fit on F^2	1.058
Final R indices [I>2σ(I)]	R_1 = 0.0360, wR_2 = 0.0958
R indices (all data)	R_1 = 0.0390, wR_2 = 0.0983
Largest diff. peak and hole	0.258 and –0.214 e.Å^{-3}
CCDC	2195415

Table S6. Crystallographic data for ethyl 1-hydroxy-2-[(methylcarbamoyl)methyl]-1*H*-indole-3-carboxylate (**35**)



Empirical formula	$C_{14}H_{16}N_2O_4$
Formula weight	276.29
Temperature	200(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 6.2144(12) Å
	b = 30.714(5) Å
	c = 7.1614(11) Å
	β= 101.726(19)°
Volume	1338.3(4) Å^3
Z	4
Density (calculated)	1.371 Mg/m^3
Absorption coefficient	0.846 mm^{-1}
F(000)	584
Crystal size	0.40 x 0.09 x 0.03 mm^3
θ range for data collection	2.88 to 67.92°.
Index ranges	–4<=h<=7, –33<=k<=36, –8<=l<=8
Reflections collected	5655
Independent reflections	2375 [R(int) = 0.0731]
Completeness to θ = 67.25°	98.4 %
Absorption correction	Semi-empirical from equivalents
Max./ min. transmission	1.00/0.77
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2375 / 0 / 187
Goodness-of-fit on F^2	1.083
Final R indices [I>2σ(I)]	R_1 = 0.0630, wR_2 = 0.1734
R indices (all data)	R_1 = 0.0990, wR_2 = 0.2055
Largest diff. peak and hole	0.249 and –0.303 e.Å^{-3}
CCDC	1827126

Table S7. Hydrogen bonds for **39** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)–H(1)...O(12)[1]	0.90(6)	1.71(6)	2.594(4)	166(5)
N(12)–H(12)...O(8)	0.88	2.18	3.000(4)	155.7

Symmetry transformations used to generate equivalent atoms: 1–x,–y,1–z