Electronic Supplementary Information

Enantioselective Strecker-Type Reaction between Azomethine Imines and Trimethylsilyl Cyanide Catalyzed by A Cinchona Alkaloid-Derived Thiourea Bearing Multiple Hydrogen-Bonding Donors

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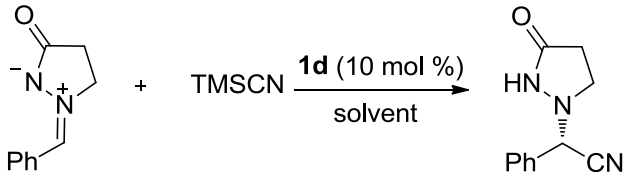
1. General methods

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out in air and using undistilled solvent, without any precautions to exclude moisture unless otherwise noted. Organic solutions were concentrated under reduced pressure on an EYELA N-1001 rotary evaporator. Reactions were monitored by thin-layer chromatography (TLC) on silica gel precoated glass plates (0.2 ± 0.03 mm thickness, GF-254, particle size 0.01–0.04 mm) from Yantai Chemical Industry Research Institute, P. R. China. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using silica gel (particle size 0.04 – 0.05 mm) from Yantai Chemical Industry Research Institute, P. R. China. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on Varian Inova (400 MHz or 300 MHz and 100 MHz or 75 MHz, respectively) spectometer. Chemical shifts (δ ppm) are relative to the resonance of the deuterated solvent as the internal standard ($CDCl_3$, δ 7.26 ppm for proton NMR, δ 77.23 ppm for carbon NMR; DMSO-d_6, δ 2.50 ppm for proton NMR, δ 39.52 ppm for carbon NMR). ^{1}H NMR data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constants (J) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). IR spectra were recorded on a Varian 1000 FT-IR spectrometer. Mass spectra were carried out using Agilent 6120 Quadrupole LC/MS system with ESI resource. High-resolution mass spectra (HRMS) for all the compounds were determined on Micromass GCT-TOF mass spertrometer with ESI resource. High performance liquid chromatography (HPLC) was performed on an Agilent 1200 Series chromatographs using a AD-H. X-ray data were recorded on a Rigaku Mercury CCD/AFC diffractomrter. Optical rotations are reported as follows: $[\alpha]_D^{25}$ (c in g per 100 mL, solvent).

2. Experimental section

Table S1 Effect of solvents

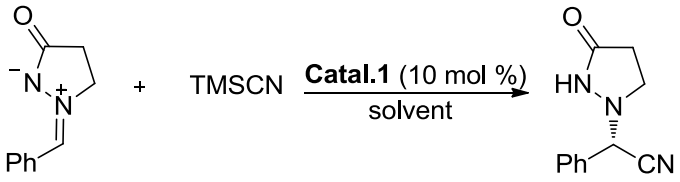


2a **3** **4a**

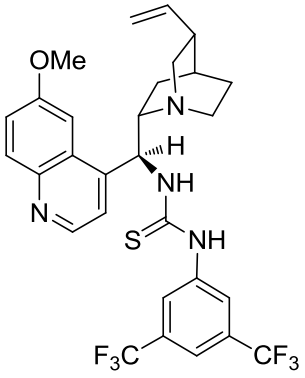
entry[a]	solvents	time(min)	yield(%)[b]	ee(%)[c]
1	1,4-Dioxane	45	94	67
2	THF	45	90	25
3	Et_2O	30	92	25
4	Acetionitrile	20	89	10
5	PhCl	28	92	42
6	EtOAc	20	85	13
7	DCM	20	87	7
8	Cyclohexane	30	88	52
9	Benzene	10	76	62
10	Ethylbenzene	20	96	57
11	Isopropylbenzene	5	75	47
12	tert-Butylbenzene	20	83	36
13	o-xylene	2	98	66
14	m-xylene	45	98	63
15	p-xylene	45	95	66
16	Mesitylene	10	95	67

[a] All reactions were carried out with **2a** (0.2 mmol), **3** (0.24 mmol, 1.2 equiv) and **1d** (0.02 mmol, 10 mol %) in corresponding solvents (0.5 mL) at room temperature. [b] Isolated yields. [c] Determined by chiral HPLC (Daicel Chirapak AD-H column).

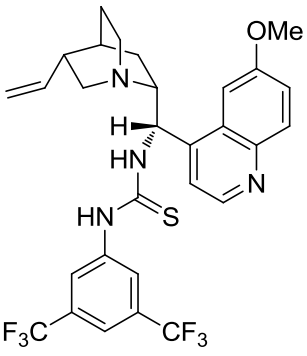
Table S2 Further investigating



2a **3** **4a**



1d



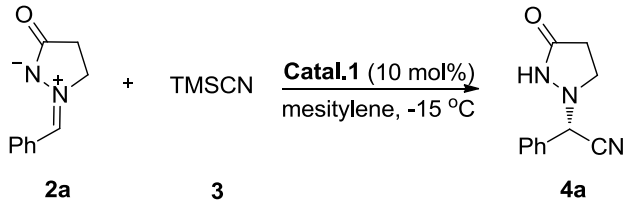
1j

entry[a]	solvents	additive[b]	temp.(°C)	time(h)	yield(%)[c]	ee(%)[d]
1	toluene	–	–20	5	99	78
2	o-xylene	–	–20	5	98	72
3	m-xylene	–	–20	5	99	74
4	mesitylene	–	–20	5	93	80

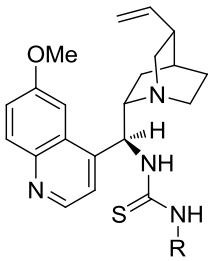
5	mesitylene	–	–15	3.5	94	79
6	mesitylene	–	–40	12	96	79
7 [e]	mesitylene	–	–40	12	90	–72
8	mesitylene	diethyl phosphite	–15	2	92	77
9	mesitylene	PhCOOH	–15	1	90	80
10	mesitylene	amino alcohol[f]	–15	3	93	79
11	mesitylene	PhOH	–15	1.5	92	81
12	mesitylene	4-$NO_2C_6H_4OH$	–15	27	93	65
13	mesitylene	4-$MeOC_6H_4OH$	–15	2.5	92	82
14	mesitylene	2-^{t}Bu-4-MeC_6H_3OH	–15	2	96	77
15	mesitylene	(*R*)-BINOL	–15	27	92	74
16	mesitylene	(*S*)-BINOL	–15	27	94	86

[a] All reactions were carried out with **2a** (0.2 mmol), **3** (0.24 mmol, 1.2 equiv) and **1d** (0.02 mmol, 10 mol %) in mesitylene (0.5 mL). [b] 10 mol % additive was used. [c] Isolated yields. [d] Determined by chiral HPLC (Daicel Chirapak AD-H column). [e] Catalyst **1j** (10 mol %) was used instead of **1d**. [f] (1*R*, 2*S*)-(+)-2-amino-1,2-diphenylethanol was used.

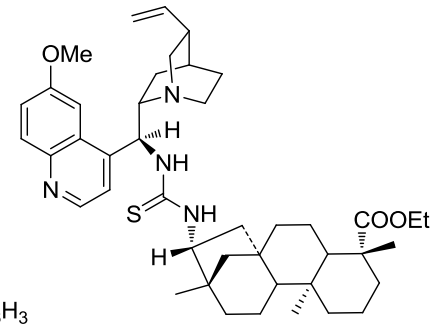
Table S3 Screening of other catalysts



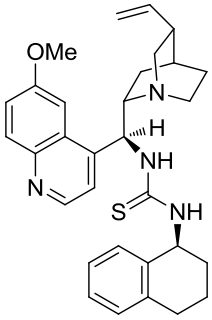
2a **3** **4a**



1k: R = 4-$NO_2C_6H_4$; **1l:** R = 2-$MeOC_6H_4$
1m: R = 4-$MeOC_6H_4$; **1n:** R = 2,6-(*i*Pr)$_2C_6H_3$
1o: R = Bn; **1p:** R = Et; **1q:** R = ^{t}Bu



1r

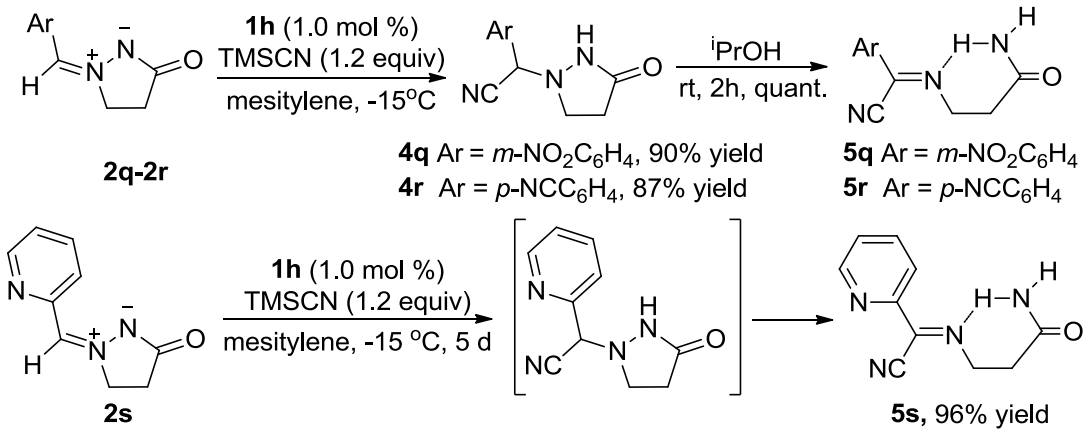


1s

entry	catalysts	solvents	temp. (°C)	time (h)	yield (%)[b]	ee (%)[c]
1	**1k**	mesitylene	–15	15	89	66
2	**1l**	mesitylene	–15	16	91	75
3	**1m**	mesitylene	–15	22	93	85
4	**1n**	mesitylene	–15	8	91	75
5	**1o**	mesitylene	–15	75	95	80
6	**1p**	mesitylene	–15	6	94	81
7	**1q**	mesitylene	–15	2	94	76
8	**1r**	mesitylene	–15	0.5	90	84
9	**1s**	mesitylene	–15	5	95	76

[a] Unless otherwise noted, reactions were carried out with **2a** (0.2 mmol), **3** (0.24 mmol, 1.2

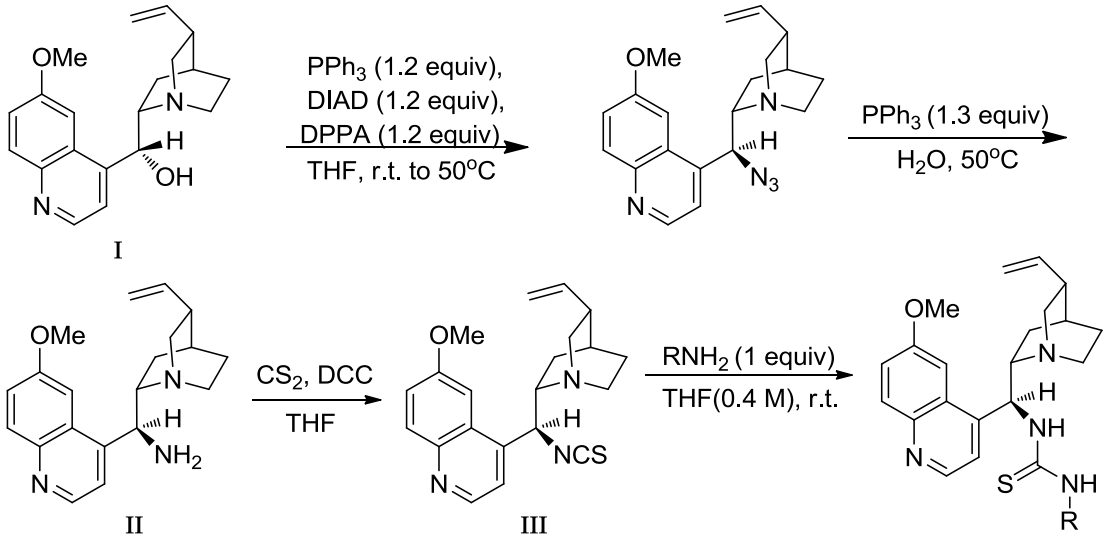
equiv) and **1** (0.02 mmol, 10 mol %) in mesitylene (0.5 mL) at –15 °C. [b] Isolated yields. [c] Determined by chiral HPLC (Daicel Chirapak AD-H column).



Scheme S1 Unexpected β-eliminative N–N bond cleavage with **2q-s** as substrates.

3. Typical experimental procedure

3.1 General procedure for the preparation of unreported quinine derived catalysts.



Catalyst **1f, 1n**, **1o**, **1p**, **1r** and **1s** which were described in this paper were prepared according to the similar reported procedures.[1,2] 9-amino (9-deoxy) epi-quinine (II) was obtained *via* the classic Mitsunobu and Staudinger reactions from Quinine (I) and subsequently transformed into isothiocyanate (III) which was used as a common electrophile in the following reactions with corresponding primary amines to give those catalysts.

3.2 General procedure for the preparation of racemic amino nitriles 4

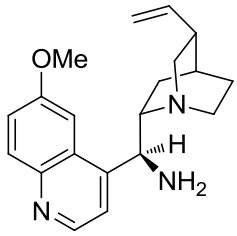
Racemic amino nitriles described in this paper were prepared by nucleophilic addition of the azomethine imines with TMSCN: the azomethine imines (0.2 mmol), TMSCN (0.24 mmol, 1.2 equiv) were combined into a vessel, 0.5 mL DCM was added *via* syringe and the system was

stirred at room temperature until the reaction was complete (detected by TLC). The solvents were evaporated under reduced pressure and the residue was purified by column chromatography on silica (*n*-hexane/ethyl acetate = 1/1) to give amino nitriles **4** as solids.

3.3 General procedure for cinchona alkaloid-derived multiple hydrogen-bonding catalyst 1h catalyzed asymmetric Strecker reaction

Azomethine imines **2** (0.2 mmol) and the catalyst **1h** (0.002 mmol, 1 mol %) were added to a vessel, to this vessel was carefully added TMSCN (30.54 μl, 1.2 equiv) in one portion at -15 ℃, after that 0.5 mL mesitylene was injected into the system *via* syringe. The system was stirred at the same temperature until the reaction was detected complete by TLC. Then 1 mL dichloromethane was added and the amino nitriles **4** were obtained after purification by flash chromatography on silica (*n*-hexane/ethyl acetate = 1/1).

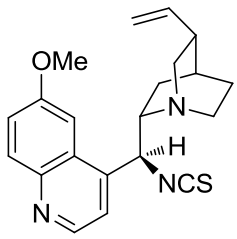
9-amino (9-deoxy) epi-quinine (II)



II

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.74 (s, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.73 – 7.51 (m, 2H), 7.50 – 7.37 (m, 1H), 6.04 – 5.79 (m, 1H), 5.18 –4.98 (m, 2H), 4.70 (d, *J* = 7.5 Hz, 1H), 3.97 (s, 3H), 3.48 – 3.25 (m, 3H), 3.18 – 2.86 (m, 5H), 2.30 (s, 1H), 2.00 (t, *J* = 13.4 Hz, 1H), 1.62 (s, 1H), 1.21 – 1.06 (m, 1H), 0.97 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 157.62, 147.67, 144.49, 140.48, 131.92, 131.60, 128.56, 121.68, 119.78, 114.56, 101.21, 62.37, 55.42, 49.32, 47.15, 39.14, 27.42, 26.42, 24.87, 23.05 ppm.

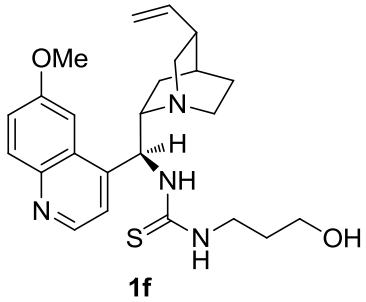
isothiocyanate (III)



III

$[\alpha]_D^{25}$ = 40.59 (c 0.17, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.68 (d, *J* = 4.5 Hz, 1H), 7.96 (d, *J* = 9.2 Hz, 1H), 7.38 (d, *J* = 4.5 Hz, 1H), 7.32 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.25 (s, 1H), 5.67 (ddd, *J* = 16.9, 10.4, 6.3 Hz, 1H), 5.40 (d, *J* = 10.0 Hz, 1H), 5.16 – 5.03 (m, 2H), 3.95 (d, *J* = 19.6 Hz, 3H), 3.78 (dd, *J* = 13.4, 10.4 Hz, 1H), 3.67 – 3.44 (m, 2H), 3.32 – 3.11 (m, 2H), 2.69 (s, 1H), 2.11 (d, *J* = 15.9 Hz, 1H), 2.05 – 1.81 (m, 3H), 1.72 – 1.57 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.10, 157.82, 147.68, 144.38, 141.83, 138.37, 131.78, 127.12, 121.40, 119.79, 116.78, 101.39, 66.46, 65.66, 57.07, 55.76, 46.12, 38.64, 27.57, 26.11, 25.38 ppm; IR (KBr) ν_{max}: 2934.6, 2379.9, 2053.5, 1627.2, 2539.8, 1236.2, 1026.3, 926.5, 846.1, 713.1, 619.4 cm^{-1}; ESI-MS (%): m/z = 366.2 $[M+H]^+$; HRMS (ESI): m/z = 366.1645 (calcd for $C_{43}H_{60}N_4O_3S+H^+$ = 366.1635).

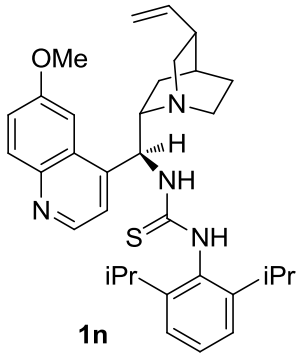
Catalyst 1f



1f

White solid; 83% yield; $[\alpha]_D^{25}$ = –135.12 (c 0.62, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.88 (s, 2H), 8.73 (d, *J* = 4.6 Hz, 1H), 8.04 (s, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.47 (s, 1H), 7.41 – 7.32 (m, 1H), 6.93 (d, *J* = 17.9 Hz, 1H), 6.74 (s, 1H), 5.74 –5.55 (m, 1H), 5.10 (dd, *J* = 13.7, 9.4 Hz, 2H), 4.11 (dd, *J* = 14.2, 7.1 Hz, 1H), 4.02 (d, *J* = 14.1 Hz, 3H), 3.83 – 3.72 (m, 1H), 3.57 (dd, *J* = 15.0, 9.4 Hz, 3H), 3.20 –3.03 (m, 1H), 3.02 – 2.88 (m, 1H), 2.66 (d, *J* = 7.8 Hz, 1H), 2.17 – 2.05 (m, 1H), 1.94 (s, 1H), 1.74 – 1.54 (m, 3H), 1.33 – 1.22 (m, 1H), 1.20 – 1.07 (m, 1H), 0.89 – 0.78 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 158.4, 147.5, 144.7, 143.2, 136.5, 131.3, 127.9, 122.7, 120.4, 117.5, 102.4, 59.8, 58.9, 55.9, 53.2, 41.5, 36.5, 32.1, 26.7, 24.5, 23.5, 22.8, 11.4; IR (KBr) ν_{max}: 3273.8, 3069.3, 2934.6, 2488.0, 1628.3, 1544.3, 1357.9, 1233.2, 1034.9, 920.1, 840.9, 673.5 cm^{-1}; ESI-MS (%): m/z = 441.2 $[M+H]^+$; HRMS (ESI): m/z = 441.2328 (calcd for $C_{24}H_{32}N_4O_2S+H^+$ = 441.2319).

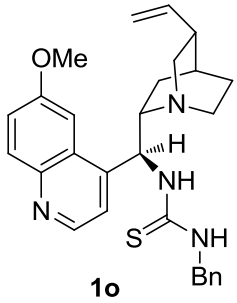
Catalyst 1n



1n

White solid; 76% yield; $[\alpha]_D^{25}$ = –90.95 (c 0.21, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.76 – 8.53 (m, 1H), 8.11 – 7.72 (m, 3H), 7.54 – 7.40 (m, 1H), 7.39 – 7.26 (m, 2H), 7.15 (d, *J* = 6.4 Hz, 1H), 7.12 – 6.95 (m, 1H), 6.52 (s, 1H), 5.84 (s, 1H), 5.64 – 5.42 (m, 1H), 5.14 – 4.97 (m, 1H), 4.88 – 4.74 (m, 1H), 3.92 (s, 3H), 3.79 – 3.52 (m, 1H), 3.40 (s, 1H), 3.24 – 3.04 (m, 2H), 3.04 – 2.89 (m, 1H), 2.89 – 2.67 (m, 2H), 2.65 – 2.45 (m, 1H), 2.39 – 2.25 (m, 1H), 2.14 (s, 1H), 1.90 – 1.78 (m, 2H), 1.39 – 1.14 (m, 6H), 1.14 – 1.04 (m, 4H), 0.98 – 0.88 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.4, 157.8, 147.8, 147.6, 147.2, 144.5, 141.0, 131.3, 130.3, 129.9, 128.8, 128.4, 124.3, 124.1, 123.4, 122.1, 118.8, 114.5, 102.5 98.4, 67.3, 61.3, 55.5, 49.1, 41.0, 39.3, 33.9, 28.7, 28.3, 27.8, 27.3, 24.9; IR (KBr) ν_{max}: 3179.9, 2945.7, 2356.9, 1629.9, 1518.8, 1238.9, 1031.5, 919.5, 841.4, 671.4 cm^{-1}; ESI-MS (%): m/z = 543.3 $[M+H]^+$; HRMS (ESI): m/z = 543.3164 (calcd for $C_{33}H_{42}N_4OS+H^+$ = 543.3152).

Catalyst 1o

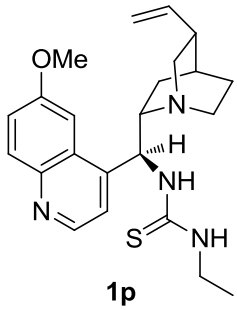


1o

White solid; 73% yield; $[\alpha]_D^{25}$ = –103.75 (c 0.32, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.98 (d, *J* = 8.9 Hz, 1H), 7.74 (s, 2H), 7.32 (dd, *J* = 23.3,

10.2 Hz, 4H), 7.15 (s, 2H), 5.63 (dd, *J* = 16.3, 8.1 Hz, 2H), 5.08 – 4.85 (m, 2H), 4.55 (s, 2H), 3.95 (s, 3H), 3.26 (s, 2H), 2.99 (d, *J* = 10.8 Hz, 2H), 2.71 (s, 1H), 2.52 – 2.16 (m, 2H), 1.89 (s, 2H), 1.60 – 1.52 (m, 1H), 1.30 (d, *J* = 11.4 Hz, 2H), 0.89 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.4, 158.0, 147.6, 144.7, 140.1, 137.5, 131.7, 128.6, 127.9, 127.6, 127.1, 122.1, 102.1, 60.8, 55.8, 54.8, 49.1, 40.9, 38.8, 33.9, 32.9, 27.1, 25.4; IR (KBr) ν_{max}: 3410.8, 2926.4, 2379.2, 1629.3, 1550.7, 1388.4, 1236.4, 1026.1, 847.5, 703.9 cm^{-1}; ESI-MS (%): m/z = 473.2 $[M+H]^+$; HRMS (ESI): m/z = 473.2382 (calcd for $C_{28}H_{32}N_4OS+H^+$ = 473.2370).

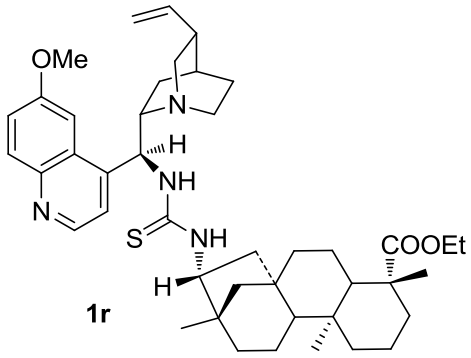
Catalyst 1p



1p

White solid; 66% yield; $[\alpha]_D^{25}$ = –94.12 (c 0.68, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (d, *J* = 3.0 Hz, 1H), 8.04 (d, J = 9.0 Hz, 1H), 7.75 (s, 1H), 7.44–7.41 (m, 1H), 7.40 – 7.38 (m, 1H), 5.79 – 5.61 (m, 2H), 5.05 – 4.98 (m, 1H), 4.98 – 4.95 (m, 1H), 4.00 (s, 3H), 3.48 – 3.13 (m, 6H), 2.88 – 2.68 (m, 3H), 2.34 (s, 1H), 1.79 – 1.55 (m, 4H), 1.44 – 1.33 (m, 1H), 1.08 – 0.97 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.9, 157.9, 147.6, 144.8, 140.8, 131.8, 127.9, 121.9, 120.2, 102.1, 60.9, 55.8, 55.3, 41.1, 39.2, 27.6, 27.3, 25.7, 14.1; IR (KBr) ν_{max}: 3313.8, 3072.2, 2932.5, 1621.5, 1544.2, 1236.3, 1031.4, 918.8, 846.8, 667.4 cm^{-1}; ESI-MS (%): m/z = 411.2 $[M+H]^+$; HRMS (ESI): m/z = 411.2223 (calcd for $C_{23}H_{30}N_4OS+H^+$ = 411.2213).

Catalyst 1r

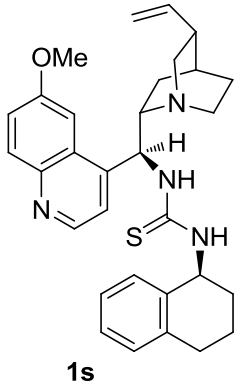


1r

White solid; 86% yield; $[\alpha]_D^{25}$ = –111.16 (c 0.86, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.02 (d, *J* = 5.3 Hz, 1H), 7.81 – 7.28 (m, 4H), 5.58 (dd, *J* = 16.7, 8.4 Hz, 1H), 5.34 (s, 1H), 4.87 (t, *J* = 12.1 Hz, 2H), 4.38 (s, 1H), 4.12 – 3.87 (m, 5H), 3.17 (dd, *J* = 25.4, 13.5 Hz, 1H), 3.01 (s, 2H), 2.65 (d, *J* = 13.6 Hz, 2H), 2.46 (s, 1H), 2.24 (s, 1H), 2.07 (d, *J* = 12.6 Hz, 1H), 1.98 (s, 1H), 1.93 – 1.68 (m, 3H), 1.60 (d, *J* = 20.6 Hz, 4H), 1.51 – 1.13 (m, 11H), 1.07 (s, 3H), 0.88 (s, 4H), 0.62 (d, *J* = 33.8 Hz, 4H), 0.43 (d, *J* = 33.8 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.8, 177.4, 171.1, 158.4, 147.7, 144.9, 141.0, 132.4, 127.6, 121.8, 120.2, 114.7, 100.9, 62.9, 60.3, 59.8, 56.7, 55.6, 55.5, 55.4, 55.2, 43.5, 41.9, 41.7, 41.1, 40.7, 40.3, 39.7, 39.5, 37.9, 37.7, 33. 7, 28.8, 27.9, 27.3, 25.5, 24.4, 21.6, 21.0, 19.9, 18.7, 14.1, 13.2; IR

(KBr) ν_{max}: 3545.5, 2941.8, 2496.3, 1950.1, 1719.7, 1544.8, 1020.6, 846.5, 741.5 cm^{-1}; ESI-MS (%): m/z = 713.5 $[M+H]^+$; HRMS (ESI): m/z = 713.4455 (calcd for $C_{43}H_{60}N_4O_3S+H^+$ = 713.4459).

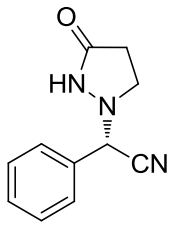
Catalyst 1s



1s

Yellow solid; 43% yield; $[\alpha]_D^{25}$ = –138.63 (c 0.81, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.1 Hz, 1H), 8.03 (d, *J* = 9.3 Hz, 1H), 7.46 – 7.29 (m, 4H), 7.18 – 7.12 (m, 2H), 7.00 (s, 1H), 5.74 – 5.58 (m, 1H), 5.37 (s, 1H), 4.97 (dd, *J* = 2.9, 1.1 Hz, 1H), 4.92 (s, 1H), 3.87 (s, 3H), 3.10 (s, 3H), 2.87 (s, 1H), 2.69 – 2.44 (m, 5H), 2.21 (s, 1H), 1.73 (s, 2H), 1.66 – 1.47 (m, 5H), 1.32 (s, 1H), 0.92 – 0.69 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.0, 158.2, 147.6, 144.8, 137.2, 135.8, 132.0, 129.2, 129.1, 128.6, 127.4, 126.1, 122.2, 120.4, 114.8, 100.8, 55.6, 54.9, 52.9, 49.1, 40.6, 39.2, 33.9, 28.8, 27.6, 27.3, 25.6, 24.9, 19.1; IR (KBr) ν_{max}: 3278.7, 3056.4, 2929.9, 2354.3, 1926.7, 1629.6, 1522.9, 1348.5, 1234.1, 1032.2, 913.7, 842.8, 739.6 cm^{-1}; ESI-MS (%): m/z = 513.3 $[M+H]^+$; HRMS (ESI): m/z = 513.2691 (calcd for $C_{31}H_{36}N_4OS+H^+$ = 513.2683).

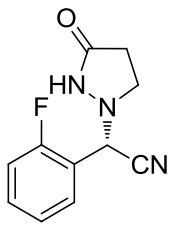
(*S*) 2-(3-oxopyrazolidin-1-yl)-2-phenylacetonitrile 4a



4a

White solid; 97% yield, 95% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 93/7, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 40.098, t (minor) = 36.087]; $[\alpha]_D^{25}$ = –107.18 (c 0.59, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.57 – 7.50 (m, 2H), 7.48 – 7.42 (m, 3H), 4.95 (s, 1H), 3.58 (s, 1H), 3.53 – 3.44 (m, 1H), 2.65 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 131.1, 129.8, 129.2, 128.3, 117.0, 62.8, 49.3, 29.8; IR (KBr) ν_{max}: 3451.3, 3189.5, 2200.1, 1692.3, 1072.1, 929.6, 699.9 cm^{-1}; ESI-MS (%): m/z = 202.1 $[M+H]^+$; HRMS (ESI): m/z = 202.0965 (calcd for $C_{11}H_{11}N_3O+H^+$ = 202.0975).

(*S*) 2-(2-fluorophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4b

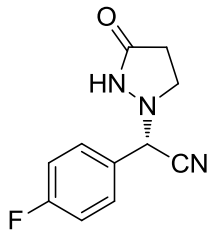


4b

White solid; 98% yield, 92% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 20.234, t (minor) = 13.614]; $[\alpha]_D^{25}$ = –89.57 (c 0.23, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (t, *J* = 7.32 Hz, 1H), 7.55 – 7.38 (m, 2H), 7.21 – 7.12 (m, 1H), 5.19 (s, 1H), 3.80 – 3.61 (m, 1H), 3.60 – 3.44 (m, 1H), 2.75 (s, 1H), 2.61 – 2.46 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.7,

158.6, 132.2, 132.1, 130.2, 124.9, 118.9, 118.7, 116.4, 116.3, 116.0, 56.5, 49.9, 29.6; IR (KBr) ν_{max}: 3460.3, 3158.1, 2848.9, 2114.2, 1697.3, 1494.7, 1094.7, 944.6, 804.9, 665.9 cm^{-1}; ESI-MS (%): m/z = 220.1 $[M+H]^+$; HRMS (ESI): m/z = 220.0881 (calcd for $C_{11}H_{10}FN_3O+H^+$ = 220.0881).

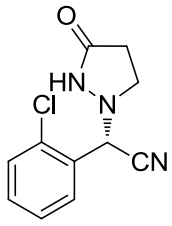
(*S*) 2-(4-fluorophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4c



4c

White solid; 95% yield, 95% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 17.480, t (minor) = 23.212]; $[\alpha]_D^{25}$ = –106.25 (c 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.42 (m, 2H), 7.12 (t, *J* = 8.44 Hz, 2H), 4.87 (s, 1H), 3.83 – 3.35 (m, 2H), 2.62 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.5, 165.0, 161.7, 130.3, 130.2, 127.0, 116.9, 116.4, 116.1, 62.1, 49.2, 29.8; IR (KBr) ν_{max}: 3457.9, 3154.4, 2020.4, 1692.9, 1422.8, 1084.5, 862.4, 638.1 cm^{-1}; ESI-MS (%): m/z = 220.1 $[M+H]^+$; HRMS (ESI): m/z = 220.0886 (calcd for $C_{11}H_{10}FN_3O+H^+$ = 220.0881).

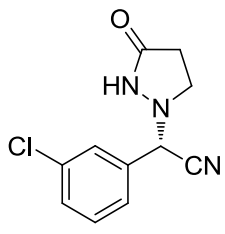
(*S*) 2-(2-chlorophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4d



4d

White solid; 98% yield, 89% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 28.720, t (minor) = 16.028]; $[\alpha]_D^{25}$ = –100.27 (c 0.38, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 1H), 7.49 – 7.43 (m, 1H), 7.42 – 7.34 (m, 2H), 5.33 (s, 1H), 3.74 – 3.57 (m, 1H), 3.55 – 3.38 (m, 1H), 2.86 – 2.69 (m, 1H), 2.67 – 2.45 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.7, 134.3, 131.4, 130.4, 130.3, 129.2, 127.6, 116.6, 59.8, 50.1, 29.7; IR (KBr) ν_{max}: 3464.8, 3168.3, 2098.8, 1708.1, 1458.9, 1040.3, 942.0, 753.5, 650.6 cm^{-1}; ESI-MS (%): m/z = 236.1 (100) and 238.1 (38) $[M+H]^+$ for ^{35}Cl and ^{37}Cl isotopic pattern; HRMS (ESI): m/z = 236.0575 (calcd for $C_{11}H_{10}ClN_3O+H^+$ = 236.0585).

(*S*) 2-(3-chlorophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4e

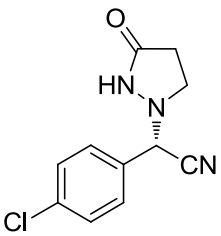


4e

White solid; 98% yield, 97% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 13.448, t (minor) = 11.605]; $[\alpha]_D^{25}$ = –105.28 (c 0.36, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.55 (s, 1H), 7.47 – 7.36 (m, 3H), 4.94 (s, 1H), 3.79 – 3.32 (m, 2H), 2.69 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.5, 135.0, 133.1, 130.5, 129.97,

128.4, 126.4, 116.6, 62.2, 49.3, 29.8; IR (KBr) ν_{max}: 3476.6, 3186.5, 2239.4, 1694.9, 1427.8, 1083.6, 1016.779, 892.2, 677.9, cm^{-1}; ESI-MS (%): m/z = 236.1 (100) and 238.1 (38) $[M+H]^+$ for ^{35}Cl and ^{37}Cl isotopic pattern; HRMS (ESI): m/z = 236.0582 (calcd for $C_{11}H_{10}ClN_3O+H^+$ = 236.0585).

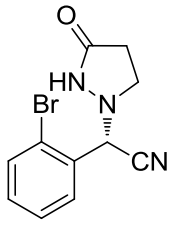
(*S*) 2-(4-chlorophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4f



4f

White solid; 99% yield, 93% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 28.720, t (minor) = 16.028]; $[\alpha]_D^{25}$ = –110.94 (c 0.32, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.34 (m, 4H), 4.90 (s, 1H), 3.76 – 3.37 (m, 2H), 2.90 – 2.42 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.5, 135.9, 129.6, 129.4, 116.6, 62.3, 49.4, 29.7; IR (KBr) ν_{max}: 3449.7, 3173.0, 2238.9, 1685.2, 1408.2 1088.1, 858.3, 685.3 cm^{-1}; ESI-MS (%): m/z = 236.1 (100) and 238.1 (38) $[M+H]^+$ for ^{35}Cl and ^{37}Cl isotopic pattern; HRMS (ESI): m/z = 236.0574 (calcd for $C_{11}H_{10}ClN_3O+H^+$ = 236.0585).

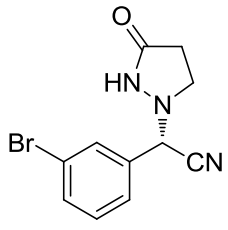
(*S*) 2-(2-bromophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4g



4g

White solid; 99% yield, 87% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 210.8 nm, t (major) = 17.439, t (minor) = 12.347]; $[\alpha]_D^{25}$ = –50.57 (c 0.44, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.70 (d, *J* = 7.68 Hz, 1H), 7.65 (d, *J* = 7.96 Hz, 1H), 7.48 – 7.38 (m, 1H), 7.37 – 7.28 (m, 1H), 5.30 (s, 1H), 3.76 – 3.58 (m, 1H), 3.53 – 3.35 (m, 1H), 2.90 – 2.68 (m, 1H), 2.66 – 2.43 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.6, 133.6, 131.5, 130.7, 130.3, 128.1, 124.5, 116.6, 62.0, 49.9, 29.6; IR (KBr) ν_{max}: 3467.6, 3187.1, 2239.9, 1693.9, 1431.2, 1024.3, 943.8, 758.2 cm^{-1}; ESI-MS (%): m/z = 280.0 (94) and 282.0 (100) $[M+H]^+$ for ^{79}Br and ^{81}Br isotopic pattern; HRMS (ESI): m/z = 280.0072 (calcd for $C_{11}H_{10}BrN_3O+H^+$ = 280.0080).

(*S*) 2-(3-bromophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4h

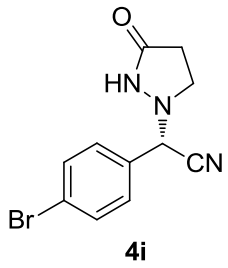


4h

White solid; 99% yield, 95% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 12.783, t (minor) = 18.109]; $[\alpha]_D^{25}$ = –72.80 (c 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (bs, 1H), 7.69 (s, 1H), 7.56 (d, *J* = 7.52 Hz, 1H), 7.48 (d, *J* = 7.32 Hz, 1H), 7.39 – 7.29 (m, 1H), 4.93 (s, 1H), 3.81 – 3.26 (m, 2H), 2.68 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 133.2, 132.8, 131.13, 130.6, 126.8, 123.0, 116.4, 62.1, 49.3, 29.7; IR (KBr) ν_{max}: 3451.6, 3167.0, 2239.5, 1689.2, 1418.0, 1079.1, 936.9, 874.7, 785.5 cm^{-1}; ESI-MS (%): m/z = 280.0

(94) and 282.0 (100) $[M+H]^+$ for ^{79}Br and ^{81}Br isotopic pattern; HRMS (ESI): m/z = 280.0069 (calcd for $C_{11}H_{10}BrN_3O+H^+$ = 280.0080).

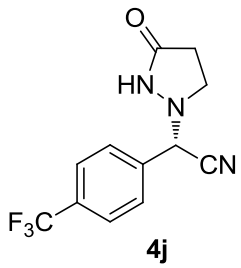
(*S*) 2-(4-bromophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4i



4i

White solid; 97% yield, 97% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 12.783, t (minor) = 18.109]; $[\alpha]_D^{25}$ = –96.36 (c 0.33, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.56 (d, *J* = 8.28 Hz, 2H), 7.40 (d, *J* = 8.20 Hz, 2H), 4.92 (s, 1H), 3.84 – 3.20 (m, 2H), 2.63 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 132.6, 130.4, 130.1, 124.4, 116.8, 62.6, 50.2, 29.9; IR (KBr) ν_{max}: 3436.8, 3150.1, 2293.6, 1679.7, 1481.3, 1080.1, 937.5, 865.1, 718.5 cm^{-1}; ESI-MS (%): m/z = 280.0 (94) and 282.0 (100) $[M+H]^+$ for ^{79}Br and ^{81}Br isotopic pattern; HRMS (ESI): m/z = 280.0074 (calcd for $C_{11}H_{10}BrN_3O+H^+$ = 280.0080).

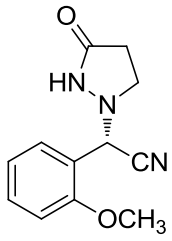
(*S*) 2-(3-oxopyrazolidin-1-yl)-2-(4-(trifluoromethyl)phenyl)acetonitrile 4j



4j

White solid; 90% yield, 90% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 210.8 nm, t (major) = 9.580, t (minor) = 12.821]; $[\alpha]_D^{25}$ = –78.18 (c 0.17, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (bs, 1H), 7.78 – 7.62 (m, 4H), 5.03 (s, 1H), 3.79 – 3.28 (m, 2H), 2.65 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 135.2, 132.4, 132.1, 129.0, 128.9, 126.4, 126.4, 125.2, 122.5, 116.6, 62.8, 50.0, 29.9; IR (KBr) ν_{max}: 3439.2, 3176.1, 2238.4, 1689.9, 1421.8, 1328.1, 1016.7, 937.6, 875.0, 808.2, 659.6 cm^{-1}; ESI-MS (%): m/z = 270.1 $[M+H]^+$; HRMS (ESI): m/z = 270.0840 (calcd for $C_{12}H_{10}F_3N_3O+H^+$ = 270.0849).

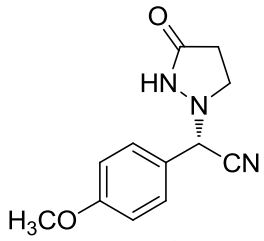
(*S*) 2-(2-methoxyphenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4k



4k

White solid; 95% yield, 90% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 34.166, t (minor) = 16.694]; $[\alpha]_D^{25}$ = –114.38 (c 0.32, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.40 Hz, 1H), 7.48 – 7.37 (m, 1H), 7.11 – 7.01 (m, 2H), 6.93 (d, *J* = 8.28 Hz, 1H), 5.29 (s, 1H), 3.87 (s, 3H), 3.71 – 3.58 (m, 1H), 3.55 – 3.41 (m, 1H), 2.69 (s, 1H), 2.59 – 2.40 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.5, 156.8, 131.5, 129.8, 120.9, 119.5, 117.3, 111.2, 56.4, 55.9, 50.0, 29.7; IR (KBr) ν_{max}: 3491.6, 3168.8, 2835.1, 2032.4, 1706.6, 1471.0, 1095.6, 1021.8, 837.7, 749.8, 654.9 cm^{-1}; ESI-MS (%): m/z = 232.1 $[M+H]^+$; HRMS (ESI): m/z = 232.1072 (calcd for $C_{12}H_{13}N_3O_2+H^+$ = 232.1081).

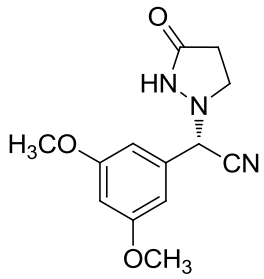
(*S*) 2-(4-methoxyphenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4l



4l

White solid; 97% yield, 83% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 15.166, t (minor) = 23.874]; $[\alpha]_D^{25}$ = –96.99 (c 0.47, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (brs, 1H), 7.43 (d, *J* = 8.04 Hz, 2H), 6.94 (d, *J* = 8.00 Hz, 2H), 4.89 (s, 1H), 3.82 (s, 3H), 3.59 – 3.32 (m, 2H), 2.60 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 160.6, 129.7, 122.9, 117.1, 114.5, 62.2, 55.4, 49.1, 29.7; IR (KBr) ν_{max}: 3449.0, 3180.1, 2230.0, 1683.8, 1407.6, 1249.5, 1023.7, 841.1, 647.9 cm^{-1}; ESI-MS (%): m/z = 232.1 $[M+H]^+$; HRMS (ESI): m/z = 232.1075 (calcd for $C_{12}H_{13}N_3O_2+H^+$ = 232.1081).

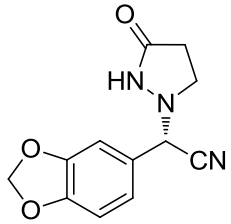
(*S*) 2-(3, 5-dimethoxyphenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4m



4m

White solid; 98% yield, 90% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 21.059, t (minor) = 24.922]; $[\alpha]_D^{25}$ = –80.44 (c 0.23, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (d, *J* = 1.36 Hz, 2H), 6.49 (s, 1H), 4.84 (s, 1H), 3.82 (s, 6H), 3.68 – 3.41 (m, 2H), 2.65 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.3, 161.2, 133.2, 116.8, 106.1, 101.6, 62.9, 55.5, 49.3, 29.8; IR (KBr) ν_{max}: 3446.5, 3158.5, 2243.6, 1687.8, 1461.5, 1065.4, 834.4, 747.1, 690.9 cm^{-1}; ESI-MS (%): m/z = 262.1 $[M+H]^+$; HRMS (ESI): m/z = 262.1175 (calcd for $C_{13}H_{15}N_3O_3+H^+$ = 262.1186).

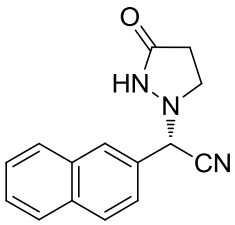
(*S*) 2-(benzo[d][1,3]dioxol-5-yl)-2-(3-oxopyrazolidin-1-yl)acetonitrile 4n



4n

Yellow solid; 93% yield, 85% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 210.8 nm, t (major) = 20.523, t (minor) = 22.498]; $[\alpha]_D^{25}$ = –94.81 (c 0.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (bs, 1H), 7.06 – 6.92 (m, 2H), 6.83 (d, *J* = 7.68 Hz, 1H), 6.01 (s, 2H), 4.82 (s, 1H), 3.70 – 3.32 (m, 2H), 2.64 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.4, 148.9, 148.4, 124.7, 122.2, 116.8, 112.6, 108.5, 101.7, 62.6, 49.7, 29.7; IR (KBr) ν_{max}: 3433.7, 3155.1, 2292.3, 1960.2, 1683.0, 1498.2, 1240.9, 1031.9, 921.4, 797.9 cm^{-1}; ESI-MS (%): m/z = 246.1 $[M+H]^+$; HRMS (ESI): m/z = 246.0868 (calcd for $C_{12}H_{11}N_3O_3+H^+$ = 246.0873).

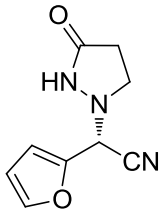
(*S*) 2-(naphthalen-2-yl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4o



4o

White solid; 99% yield, 87.3% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 14.979, t (minor) = 17.002]; $[\alpha]_D^{25}$ = -83.14 (c 0.26, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.94 – 7.77 (m, 3H), 7.54 (d, *J* = 5.76 Hz, 3H), 5.07 (s, 1H), 3.83 – 3.29 (m, 2H), 2.62 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 133.6, 132.9, 129.2, 128.5, 128.3, 127.9, 127.8, 127.3, 126.9, 125.1, 117.0, 62.9, 49.3, 29.8; IR (KBr) ν_{max}: 33449.9, 3151.5, 3039.5, 2007.5, 1684.8, 1426.7, 1371.6, 1079.2, 859.2, 751.3, 632.9 cm^{-1}; ESI-MS (%): m/z = 252.1 $[M+H]^+$; HRMS (ESI): m/z = 252.1123 (calcd for $C_{15}H_{13}N_3O_2+H^+$ = 252.1131).

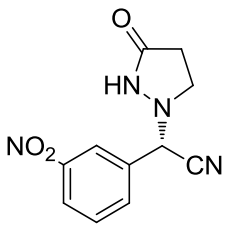
(*R*) 2-(furan-2-yl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4p



4p

White solid; 99% yield, 74% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 16.289, t (minor) = 26.215]; $[\alpha]_D^{25}$ = –66.82 (c 0.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.48 (s, 1H), 6.61 (d, *J* = 3.04 Hz, 1H), 6.48 – 6.39 (m, 1H), 4.93 (s, 1H), 3.64 (s, 1H), 3.59 – 3.48 (m, 1H), 2.50 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.7, 144.6, 144.0, 115.3, 111.9, 111.2, 56.2, 49.5, 29.6; IR (KBr) ν_{max}: 3455.6, 3151.1, 1696.0, 1499.4, 1311.8, 1072.0, 954.8, 760., 607.1 cm^{-1}; ESI-MS (%): m/z = 192.1 $[M+H]^+$; HRMS (ESI): m/z = 192.0770 (calcd for $C_9H_9N_3O_2+H^+$ = 192.0768).

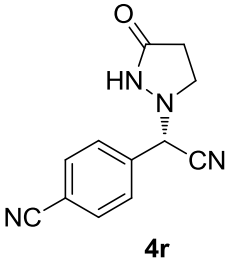
(*S*) 2-(3-nitrophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4q



4q

White solid; 90% yield; chiral GC and RPC (CH_3CN and water as eluant) also failed to detect its enantioselectivity; $[\alpha]_D^{25}$ = +99.23 (c 0.26, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.42 (s, 1H), 8.31 (d, *J* = 8.28 Hz, 1H), 7.92 (d, *J* = 7.52 Hz, 1H), 7.80 – 7.60 (m, 1H), 5.07 (s, 1H), 3.87 – 3.41 (m, 2H), 2.75 – 2.53 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.6, 148.6, 134.1, 133.4, 130.4, 124.8, 123.5, 116.0, 62.3, 50.7, 29.7; IR (KBr) ν_{max}: 3396.4, 3172.9, 2093.3, 1702.9, 1094.8, 921.3, 814.9, 669.3 cm^{-1}; ESI-MS (%): m/z = 247.1 $[M+H]^+$; HRMS (ESI): m/z = 247.0814 (calcd for $C_{11}H_{10}N_4O_3+H^+$ = 247.0826).

(*S*) 4-(cyano(3-oxopyrazolidin-1-yl)methyl)benzonitrile 4r

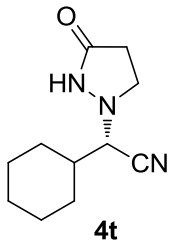


4r

White solid; 87% yield, chiral GC and RPC (CH_3CN and water as eluant) also failed to detect its enantioselectivity; $[\alpha]_D^{25}$ = –64.80 (c 0.25, $CHCl_3$); ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.99 (brs, 1H), 7.74 (d, *J* = 7.84 Hz, 2H), 7.67 (d, *J* = 7.92Hz, 2H), 4.97 (s, 1H), 3.73 – 3.39 (m, 2H), 2.88 – 2.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.6, 136.2, 132.9, 129.1, 117.9, 116.3, 113.6, 62.6, 49.9, 29.7; IR (KBr) ν_{max}: 3443.0, 3150.1, 2005.8, 1931.5, 1369.5, 1072.5, 807.5, 649.9 cm^{-1}; ESI-MS (%): m/z = 227.1 $[M+H]^+$; HRMS (ESI): m/z = 227.0920 (calcd for $C_{12}H_9N_4O+H^+$ = 227.0927).

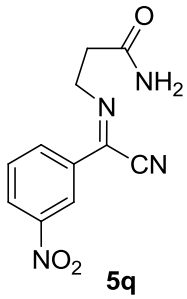
(*S*) 2-cyclohexyl-2-(3-oxopyrazolidin-1-yl) acetonitrile 4t



4t

White solid; 95% yield, 12% ee [Daicel Chiralcel AD-H, hexanes/i-PrOH = 85/15, flow rate: 1.0 mL·min^{-1}, λ = 254.4 nm, t (major) = 8.334, t (minor) = 14.499]; $[\alpha]_D^{25}$ = +31.25 (c 0.16, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 3.55 (d, *J* = 8.28 Hz, 1H), 3.47 – 3.40 (m, 2H), 2.92 – 2.48 (m, 2H), 1.98 (d, *J* = 12.08 Hz, 2H), 1.83 – 1.54 (m, 4H), 1.36 – 1.11 (m, 3H), 1.11 – 0.89 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.7, 117.7, 65.5, 50.1, 38.6, 30.1, 29.9, 29.8, 26.0, 25.4, 25.2; IR (KBr) ν_{max}: 3168.8, 2229.1, 1688.8, 1374.5, 1090.4, 741.4 cm^{-1}; ESI-MS (%): m/z = 208.1 $[M+H]^+$; HRMS (ESI): m/z = 208.1435 (calcd for $C_{11}H_{17}N_3O+H^+$ = 208.1444).

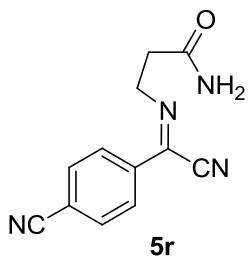
3-(cyano(3-nitrophenyl)methyleneamino)propanamide 5q



5q

White solid; >95% yield; ^1H NMR (300 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.26 (d, *J* = 25.38 Hz, 2H), 7.92 – 7.49 (m, 1H), 6.40 – 5.70 (m, 2H), 4.50 – 4.00 (m, 2H), 3.00 – 2.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 141.2, 136.6, 132.6, 128.1, 117.8, 115.7, 112.9, 109.0, 54.6, 35.7; IR (KBr) ν_{max}: 3195.2, 2256.6, 1966.3, 1649.9, 1527.4, 1425.2, 1346.1, 1095.5, 929.7, 803.4, 744.1, 689.2, 634.3 cm^{-1}; ESI-MS (%): m/z = 247.1 $[M+H]^+$; HRMS (ESI): m/z = 247.0816 (calcd for $C_{11}H_{10}N_4O_3+H^+$ = 247.0826).

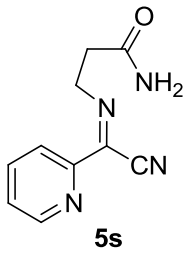
3-(cyano(4-cyanophenyl)methyleneamino)propanamide 5r



5r

White solid; >95% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.12 Hz, 2H), 7.78 (d, *J* = 9.12 Hz, 2H), 5.99 – 5.36 (m, 2H), 4.55 – 3.97 (m, 2H), 3.00 – 2.53 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 141.2, 136.6, 132.6, 128.1, 117.8, 115.7, 108.9, 54.7, 27.7; IR (KBr) ν_{max}: 3197.7, 2932.4, 2226.8, 1942.0, 1648.9, 1420.2, 1029.9. 854.7, 772.3, 644.3 cm^{-1}; ESI-MS (%): m/z = 227.1 $[M+H]^+$; HRMS (ESI): m/z = 227.0921 (calcd for $C_{12}H_9N_4O+H^+$ = 227.0927).

3-(cyano(pyridin-2-yl)methyleneamino)propanamide 5s



5s

White solid; 96% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.63 (d, J = 3.76 Hz, 1H), 7.94 – 7.73 (m, 2H), 7.54 – 7.20 (m, 2H), 6.79 (s, 1H), 4.17 – 3.79 (m, 2H), 2.60 – 2.42 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.5, 156.4, 154.8, 148.4, 143.0, 132.0, 126.3, 115.1, 59.8, 40.5; IR (KBr) ν_{max}: 3168.5, 2925.1, 2229.6, 1665.3, 1427.6, 1056.6, 924.9, 801.9, 628.7 cm^{-1}; ESI-MS (%): m/z = 203.1 $[M+H]^+$; HRMS (ESI): m/z = 203.0920 (calcd for $C_{10}H_{10}N_4O+H^+$ = 203.0927)

4. X-ray data of chiral 4h and 4i

4.1 Crystal structure determination of compound 4h:

Crystal data and structure refinement for **4h**:

Identification code	cd212477
Empirical formula	$C_{11}H_{10}BrN_3O$
Formula weight	280.13
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 5.6282(9) Å alpha = 90 deg.
	b = 9.0457(14) Å beta = 90 deg.
	c = 22.768(4) Å gamma = 90 deg.
Volume	1159.2(3) Å ^3
Z, Calculated density	4, 1.605 Mg/m^3
Absorption coefficient	3.528 mm^-1
F(000)	560
Crystal size	0.276 x 0.211 x 0.143 mm
Theta range for data collection	2.42 to 25.49 deg.
Limiting indices	-6<=h<=6, -10<=k<=10, -26<=l<=27
Reflections collected / unique	6749 / 2154 [R(int) = 0.0442]
Completeness to theta = 25.49	99.9 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.42118
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	2154 / 1 / 149
Goodness-of-fit on F^2	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1173
R indices (all data)	R1 = 0.0557, wR2 = 0.1220
Absolute structure parameter	0.008(16)
Largest diff. peak and hole	0.719 and -0.746 e.A^-3

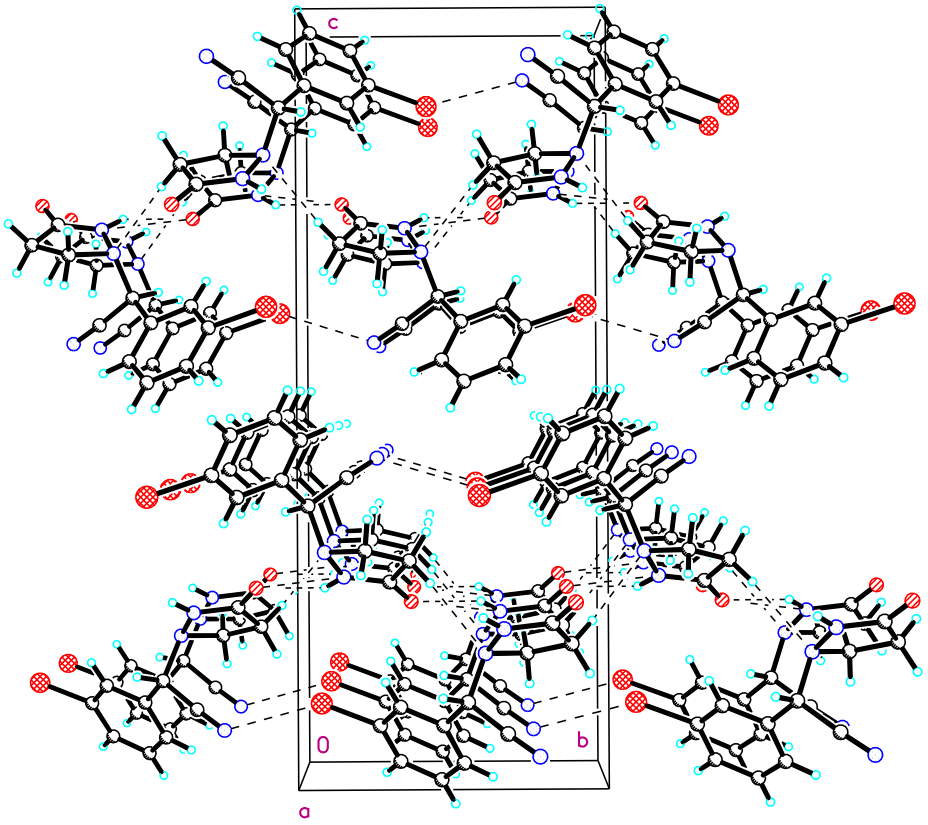


Figure S1. Packing of moleculars in a unit cell of **4h**

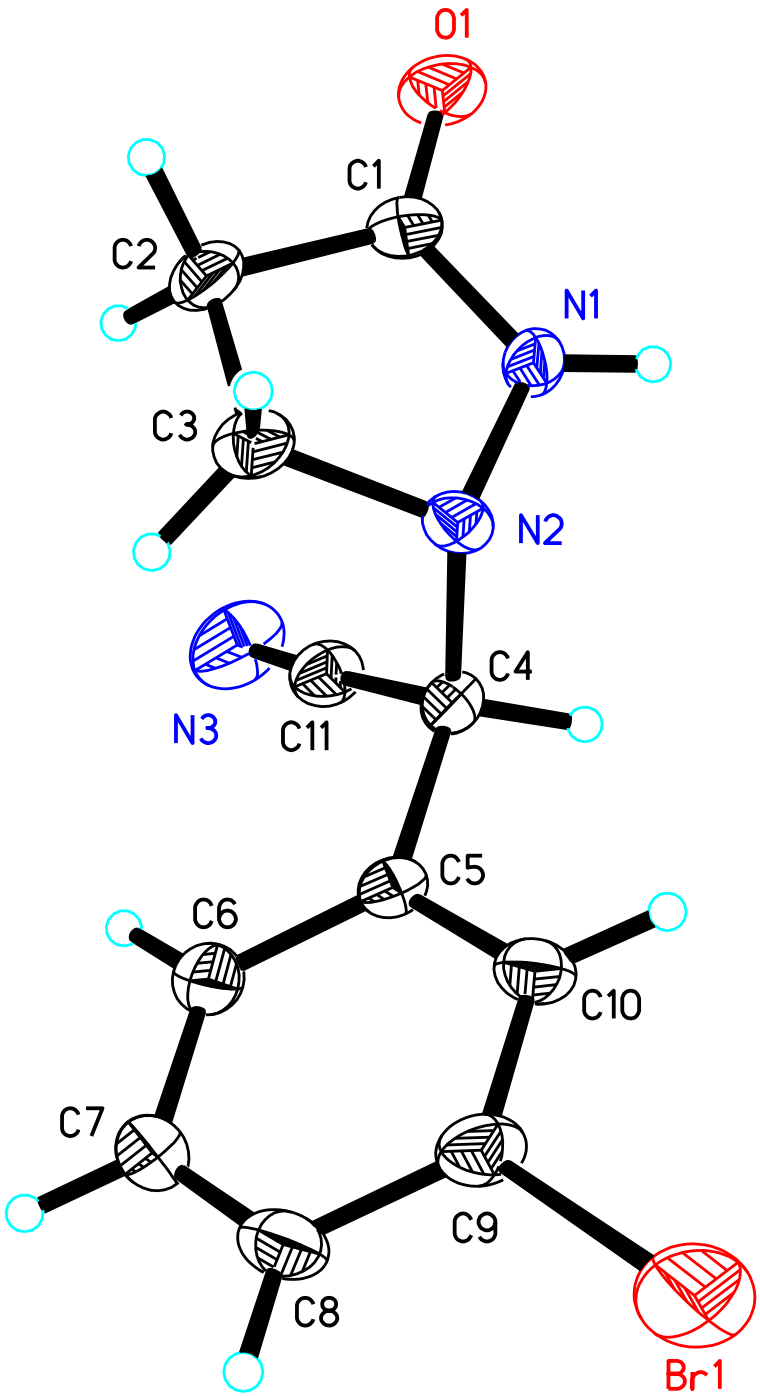


Figure S2. OPTEP drawing of **4h** (40% thermal ellipsoids)

The crystal was prepared from the solution of **4h** in DCM and n-hexane. CCDC 902498 contains

the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

4.2 Crystal structure determination of compound 4i:

Crystal data and structure refinement for **4i**:

Identification code	cd212479
Empirical formula	$C_{11}H_{10}BrN_3O$
Formula weight	280.13
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P1
Unit cell dimensions	a = 5.5927(10) Å alpha = 113.882(4) deg.
	b = 9.9073(17) Å beta = 91.874(4) deg.
	c = 11.448(2) Å gamma = 99.063(4) deg.
Volume	569.50(18) Å ^3
Z, Calculated density	2, 1.634 Mg/m^3
Absorption coefficient	3.591 mm^-1
F(000)	280
Crystal size	0.265 x 0.145 x 0.112 mm
Theta range for data collection	1.96 to 26.00 deg.
Limiting indices	-6<=h<=6, -12<=k<=10, -14<=l<=13
Reflections collected / unique	3448 / 2757 [R(int) = 0.0186]
Completeness to theta = 26.00	99.6 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.36709
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2757 / 44 / 324
Goodness-of-fit on F^2	0.947
Final R indices [I>2sigma(I)]	R1 = 0.0355, wR2 = 0.0814
R indices (all data)	R1 = 0.0523, wR2 = 0.0880
Absolute structure parameter	-0.006(7)

Largest diff. peak and hole	0.332 and -0.344 e.A^-3

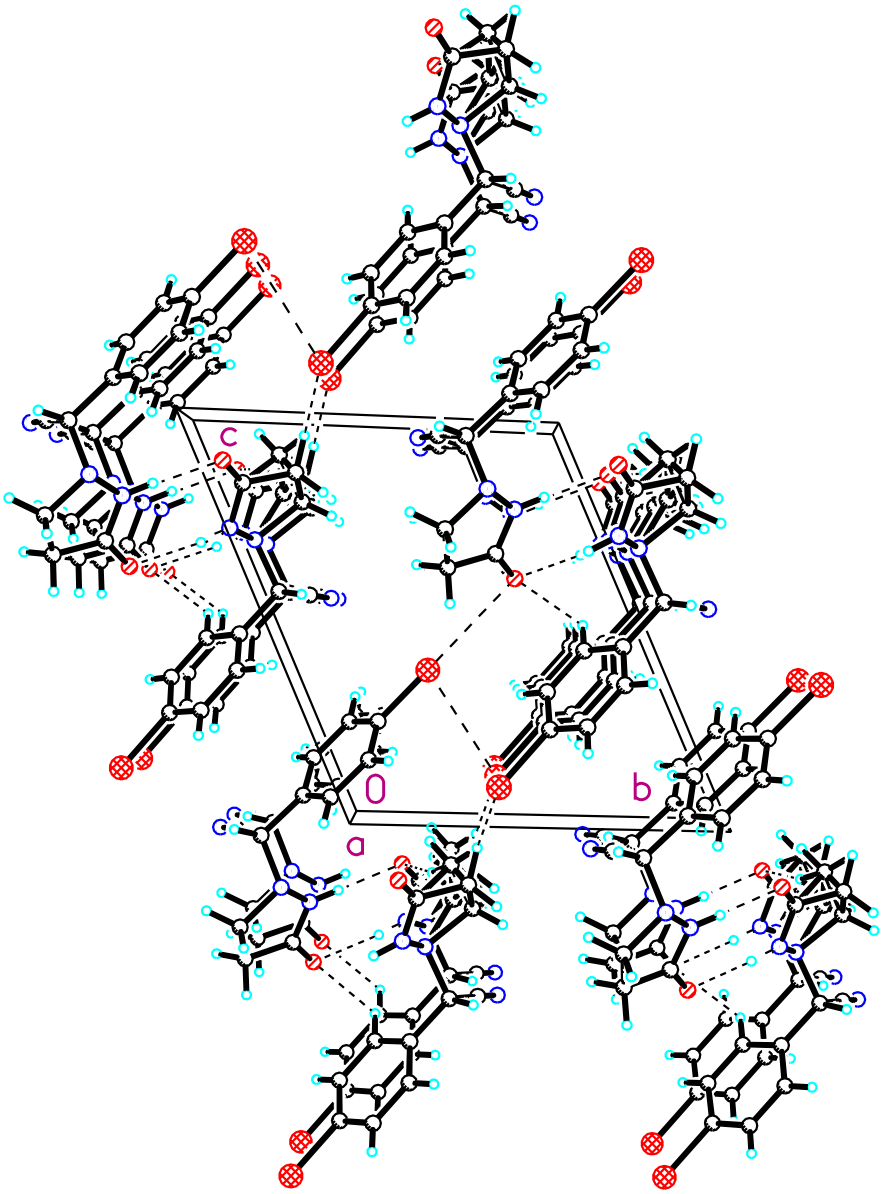


Figure S3. Packing of moleculars in a unit cell of **4i**

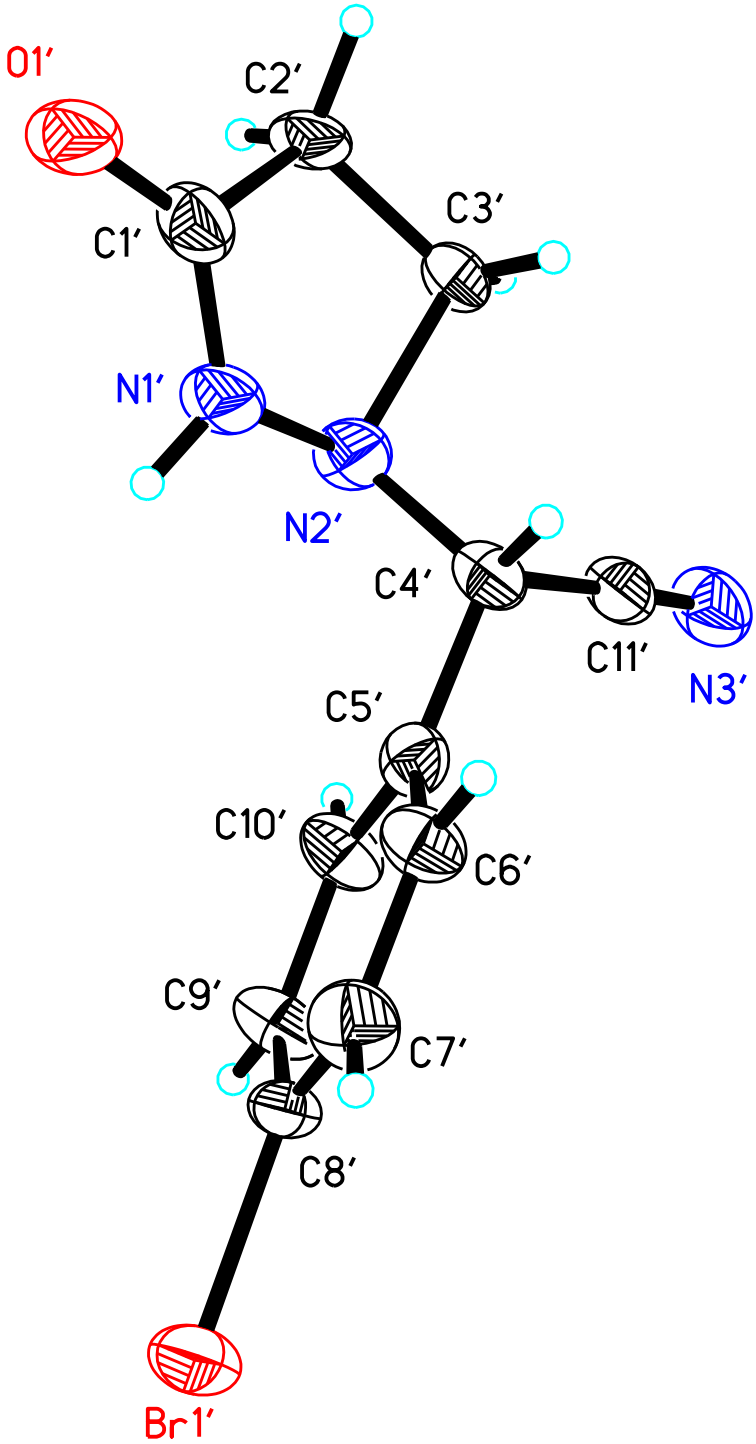


Figure S4. OPTEP drawing of **4i** (40% thermal ellipsoids)

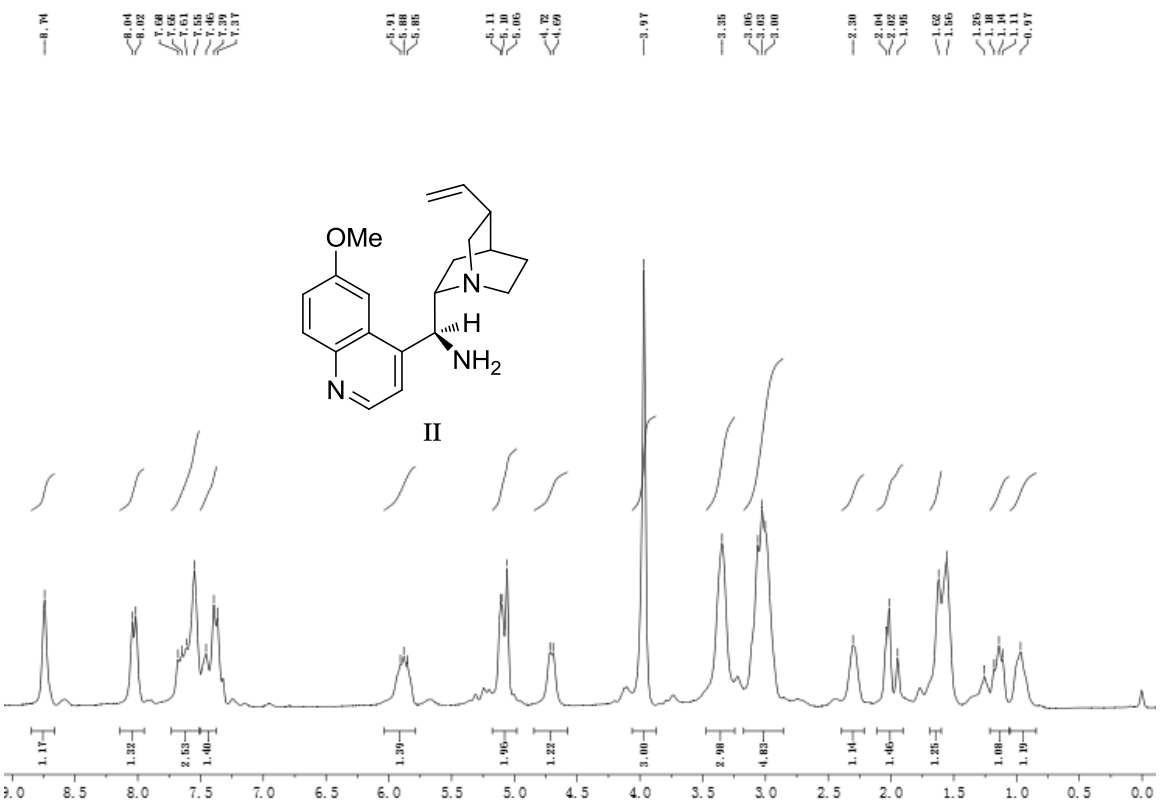
The crystal was prepared from the solution of **4i** in DCM and n-hexane. CCDC 902501 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

5. Reference

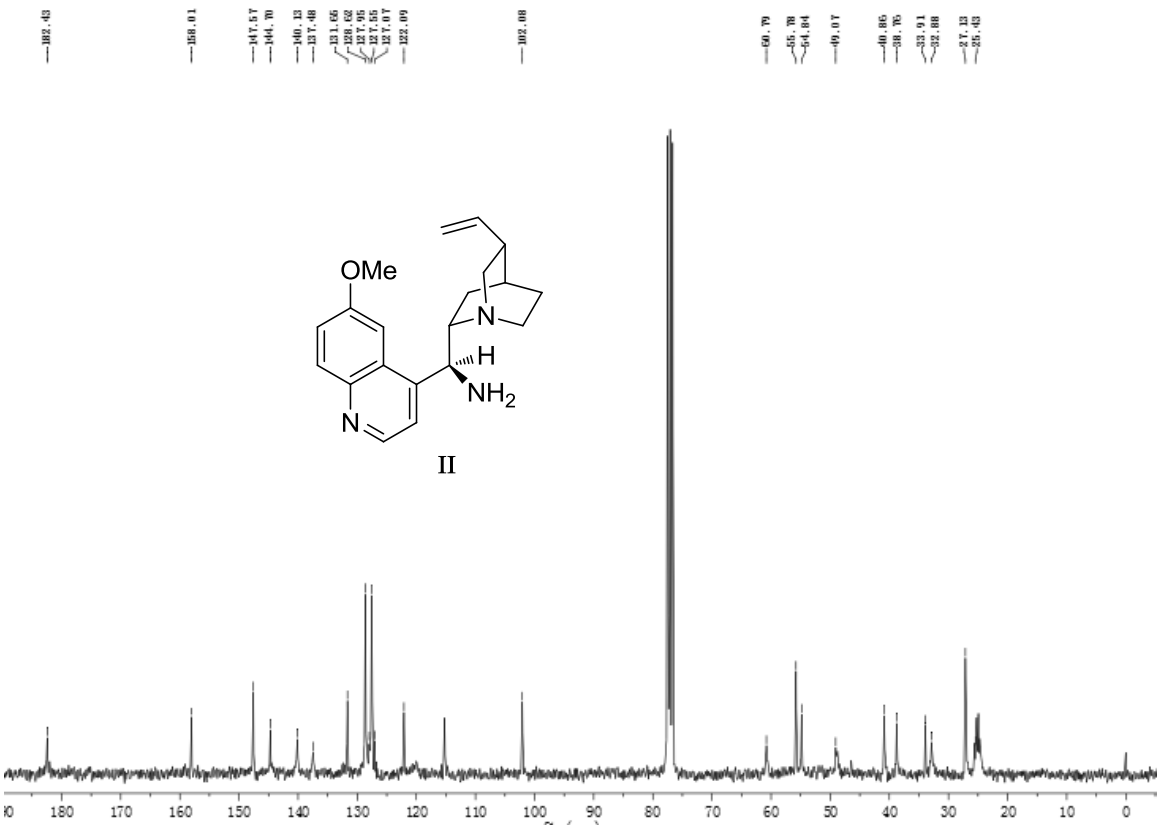
1. X. Shi, W. He, H. Li, X. Zhang, S. Y. Zhang, *Tetrahedron Lett.*, 2011, **52**, 3204.
2. M. X. Zhao, W. H. Tang, M. X. Chen, D. K. Wei, T. L. Dai, M. Shi, *Eur. J. Org. Chem.*, 2011, 6078.
3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R.Cheeseman,; J. A. Jr. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O.Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B.Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong. C. Gonzalez, J. A. Pople. *Gaussian 03*, Revision B.04; Gaussian, Inc.: Wallingford, CT, 2003.

6. ^{1}H NMR and ^{13}C NMR spectra

9-amino (9-deoxy) epi-quinine (II)

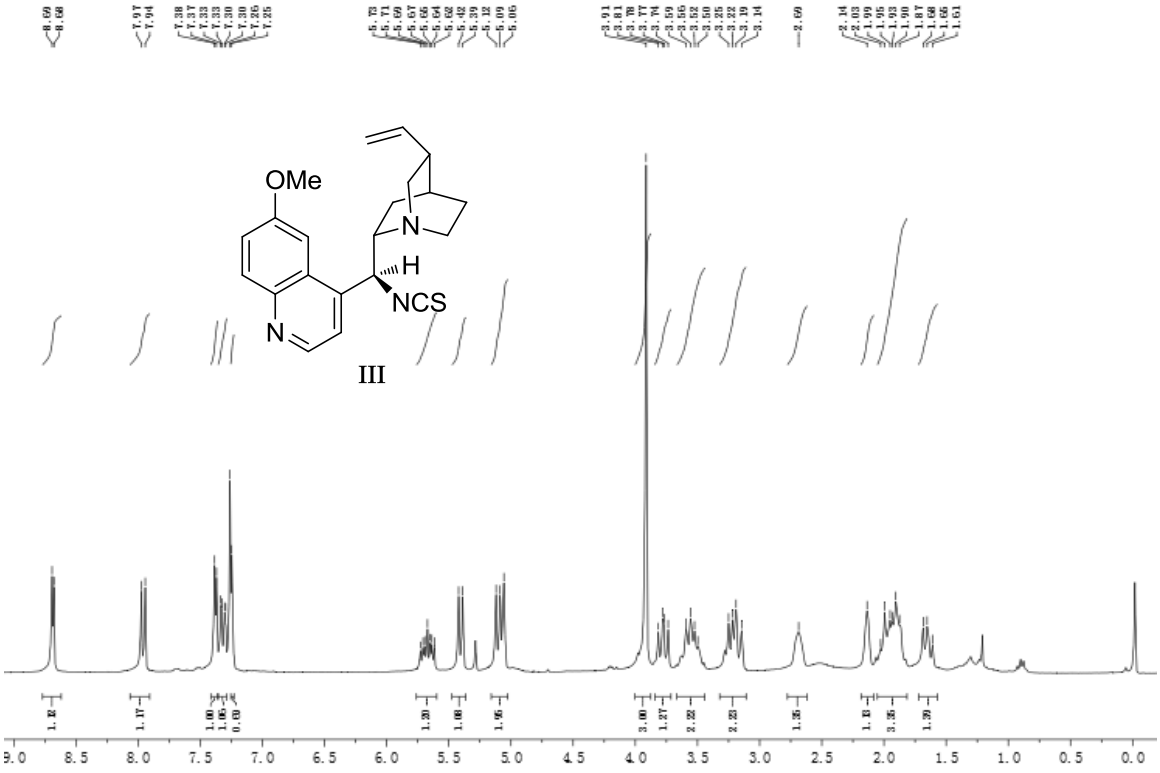


II

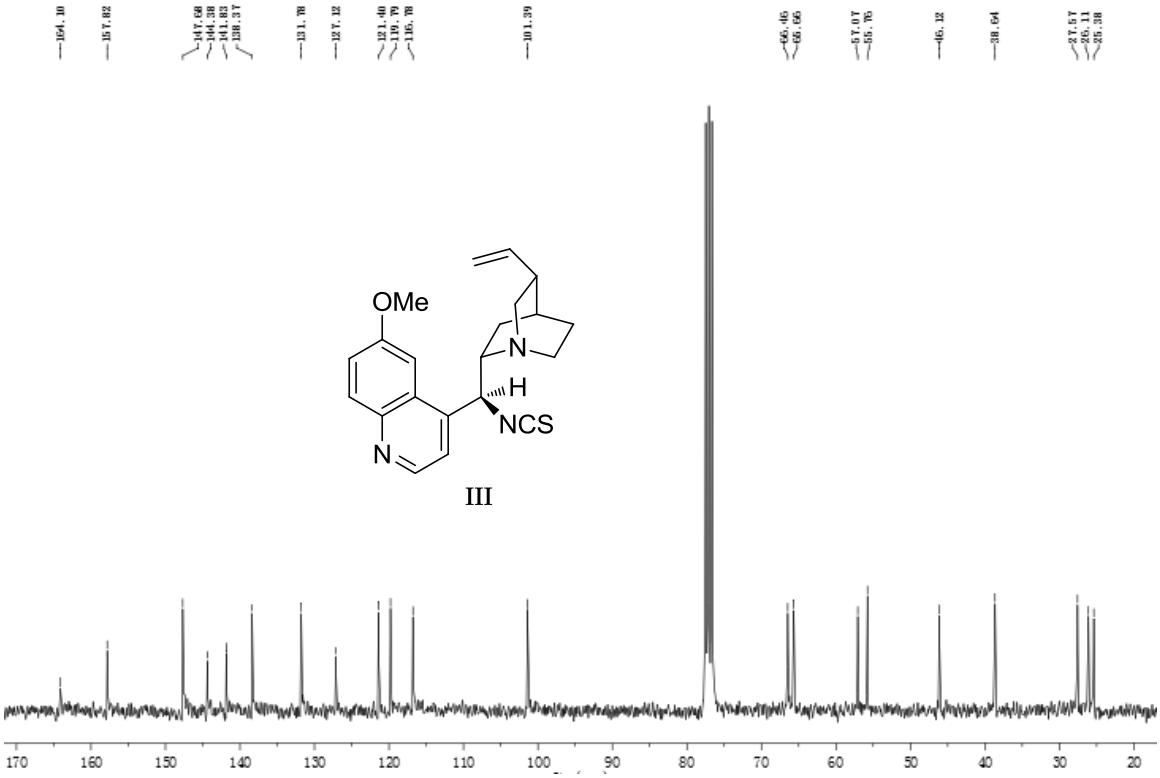


II

isothiocyanate (III)

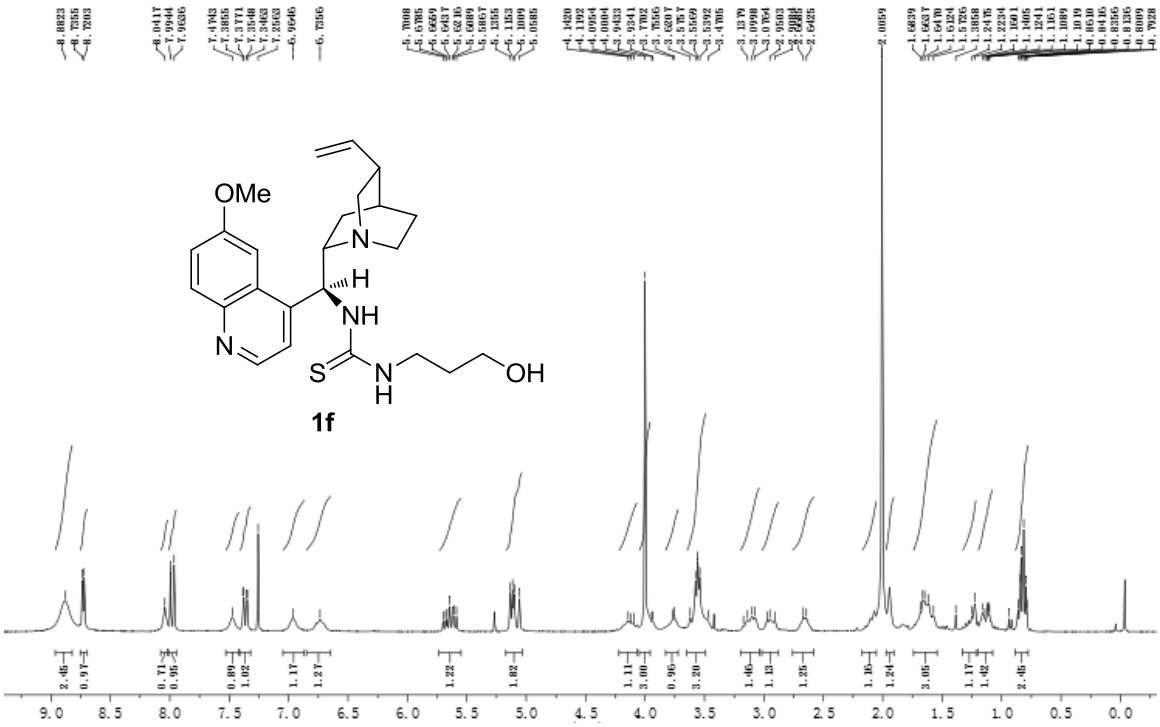


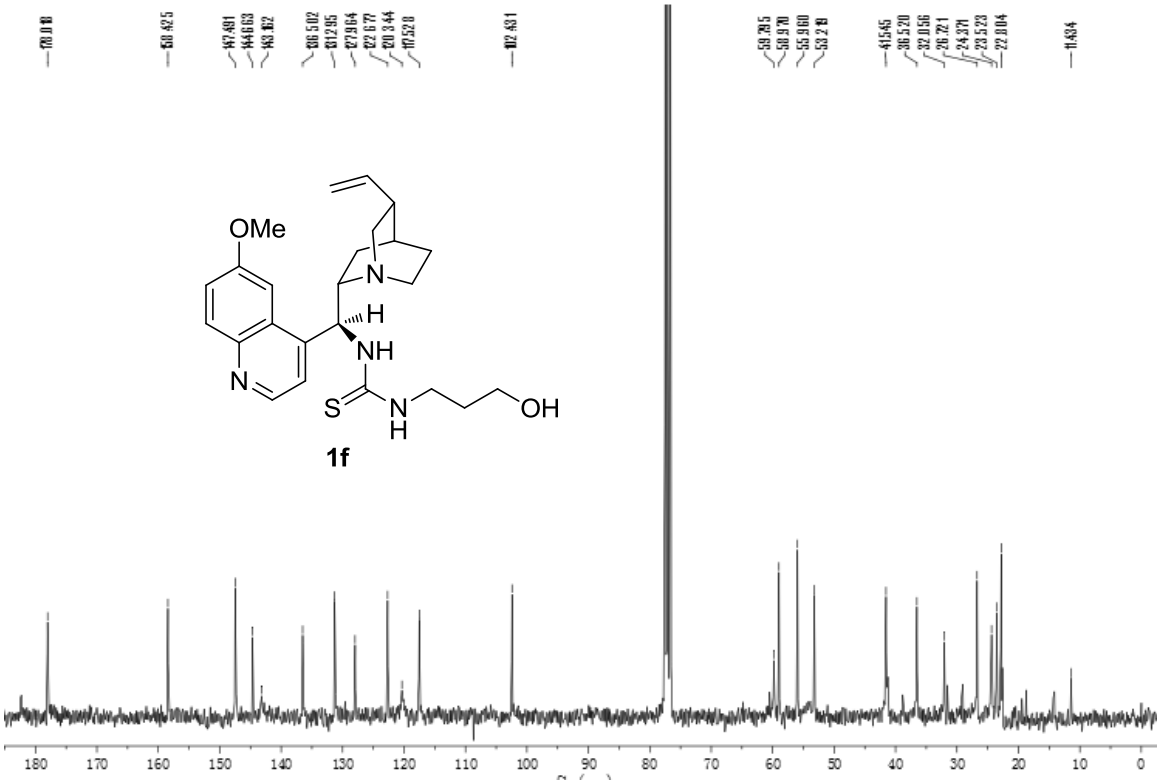
III



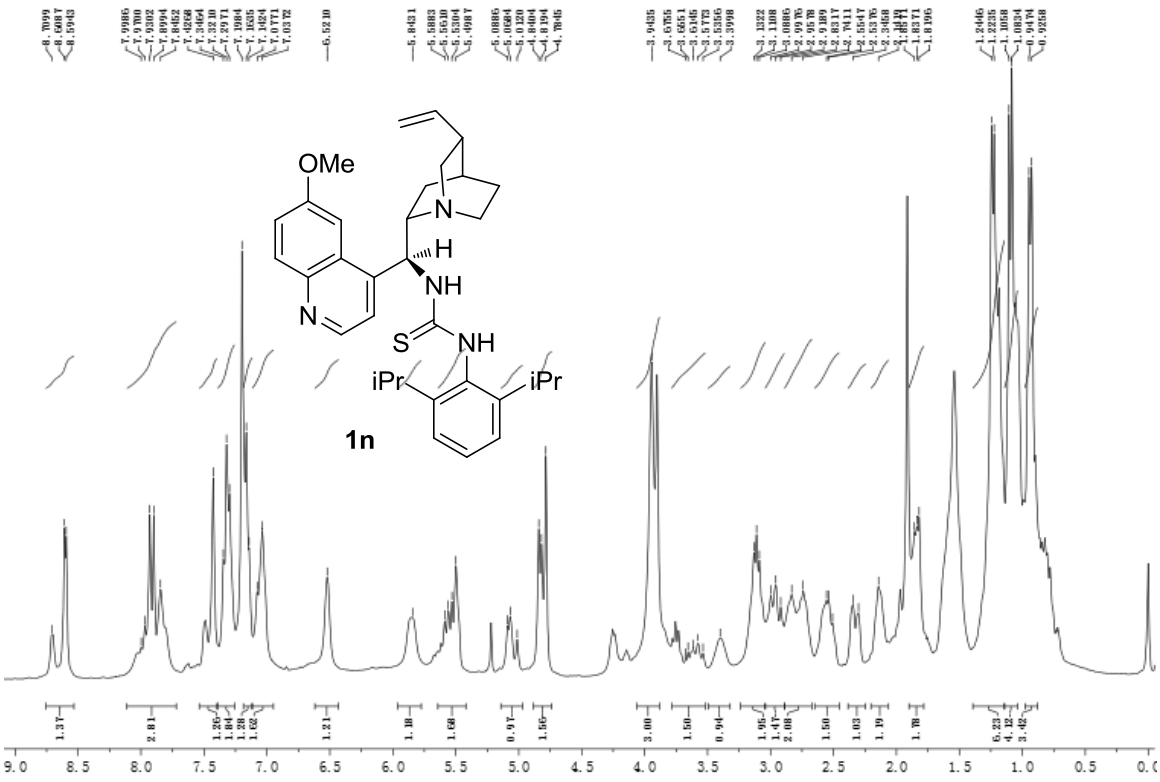
III

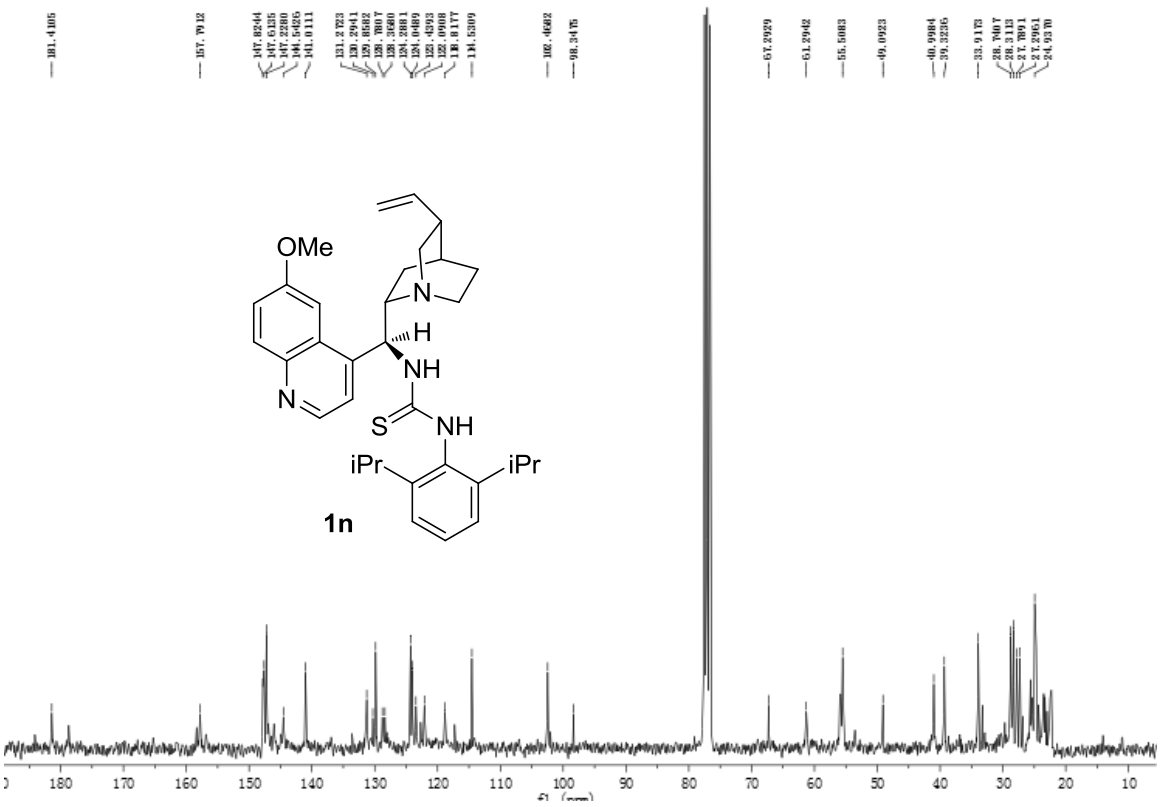
Catalyst 1f





Catalyst 1n





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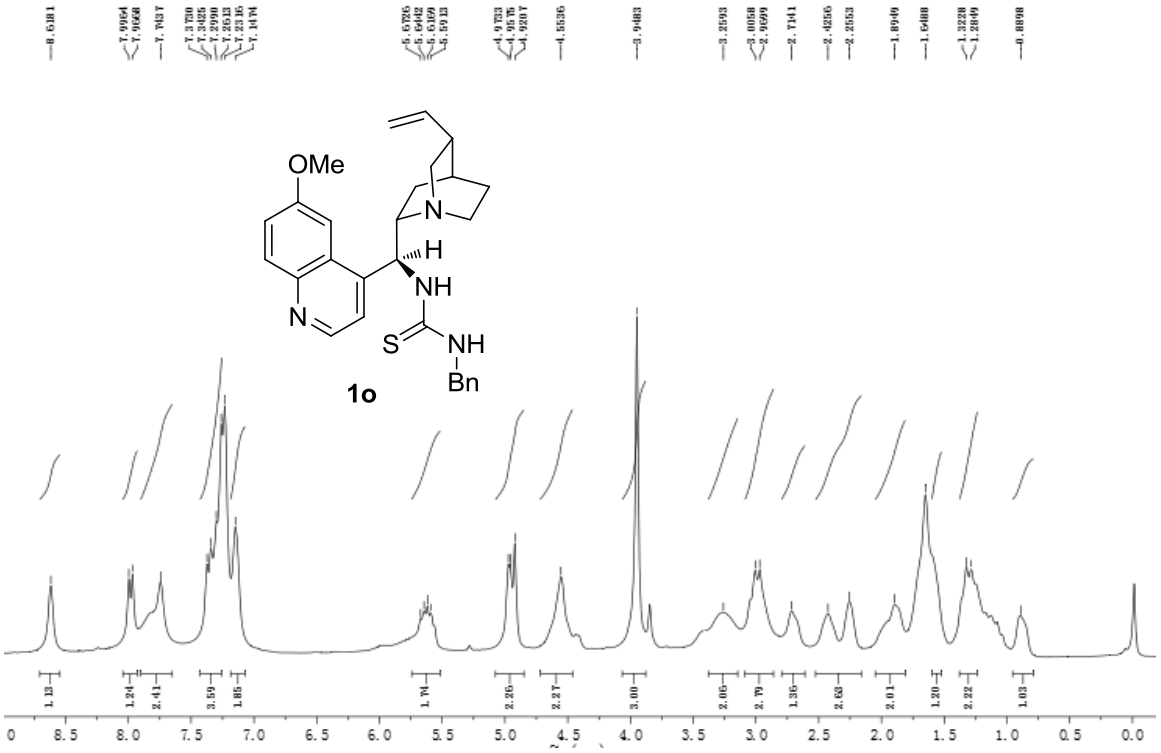

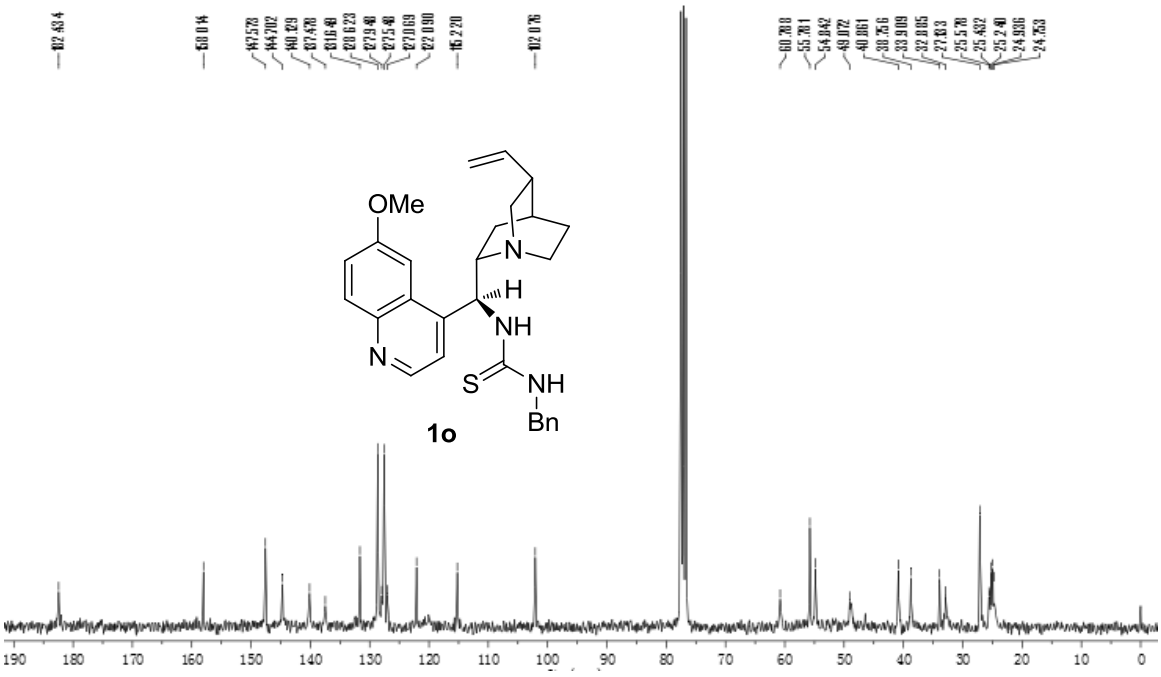

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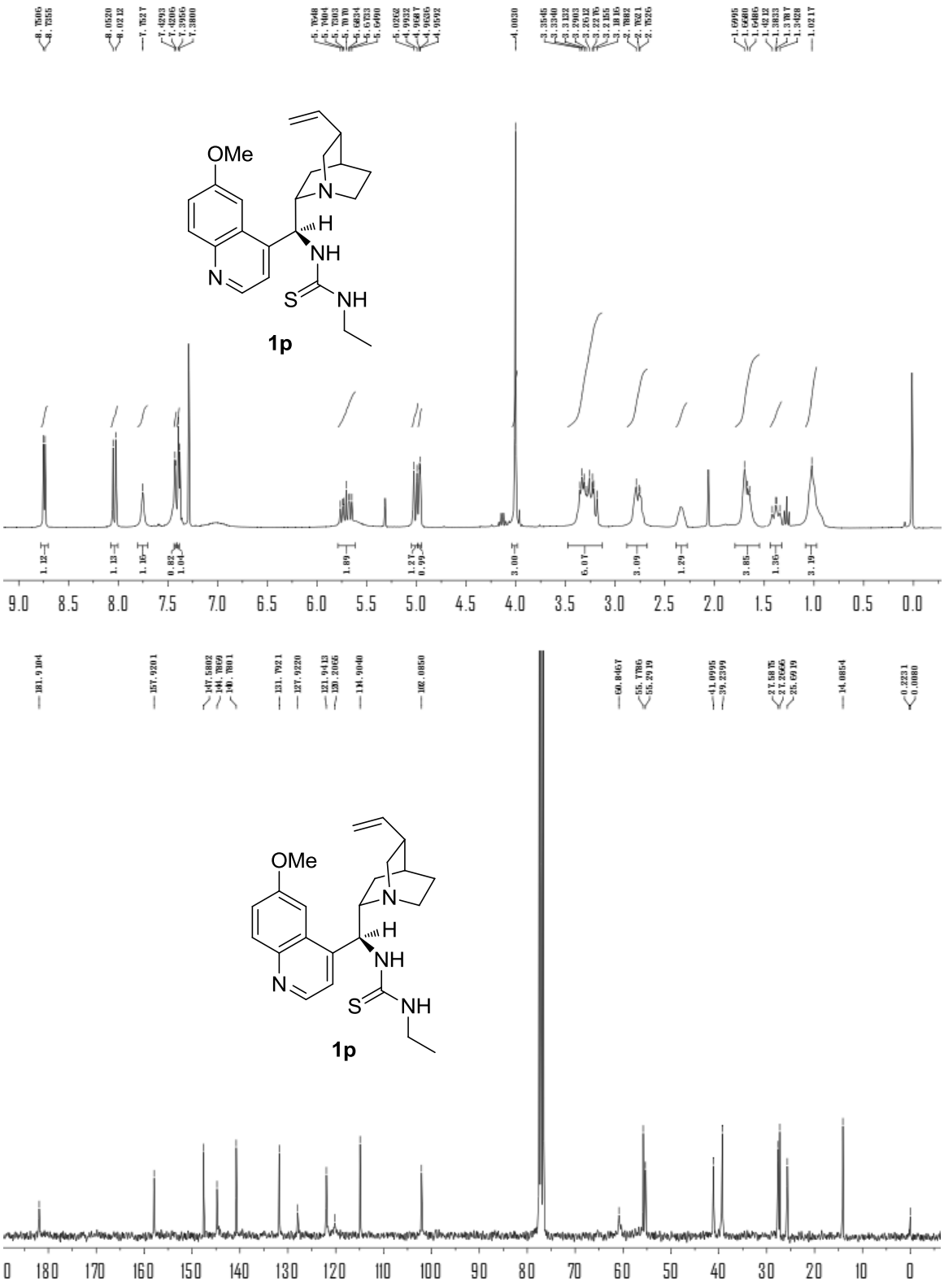
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NH
S
NH
1p
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OMe
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H
NH
S
NH
1p
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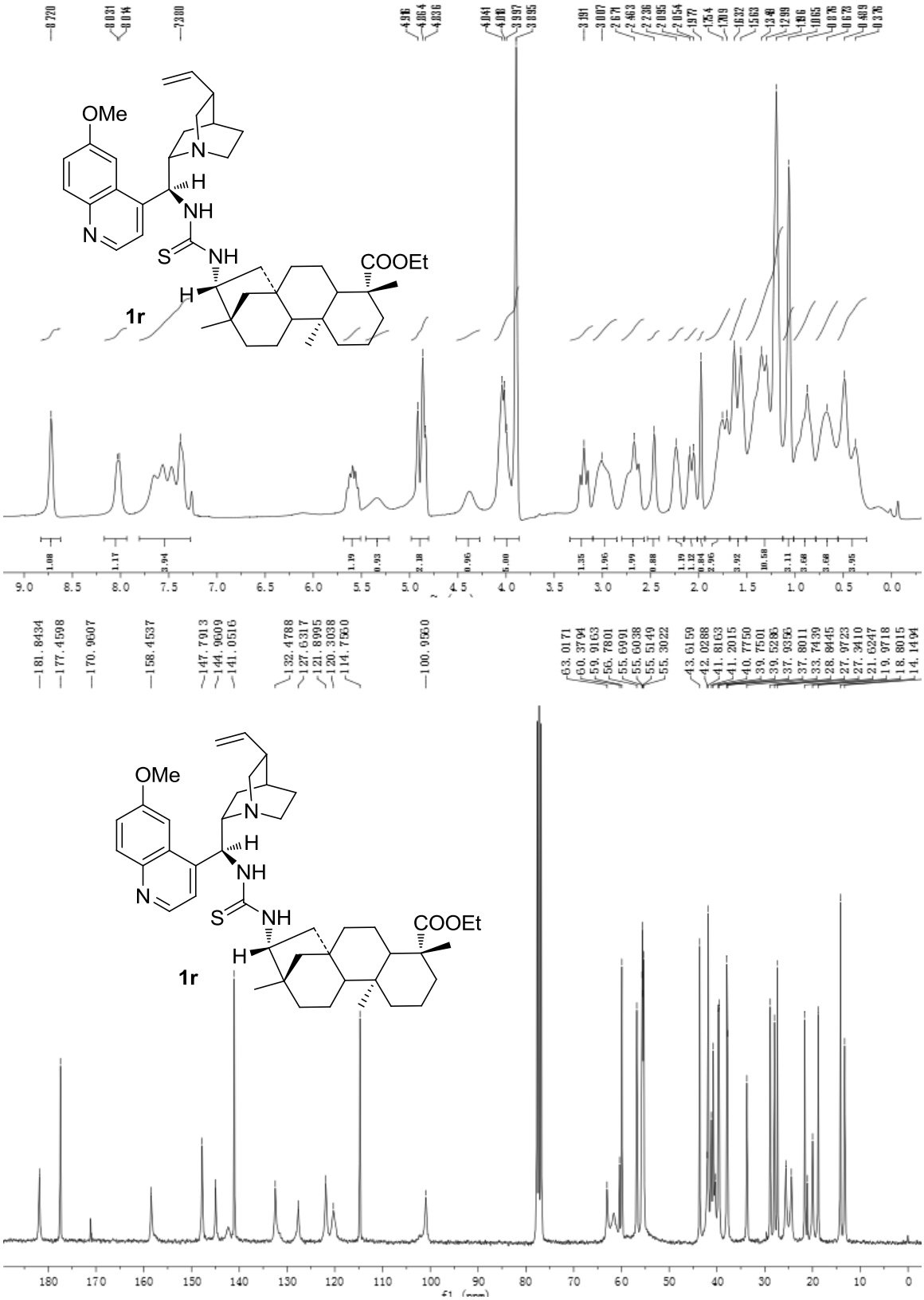
Catalyst 1r



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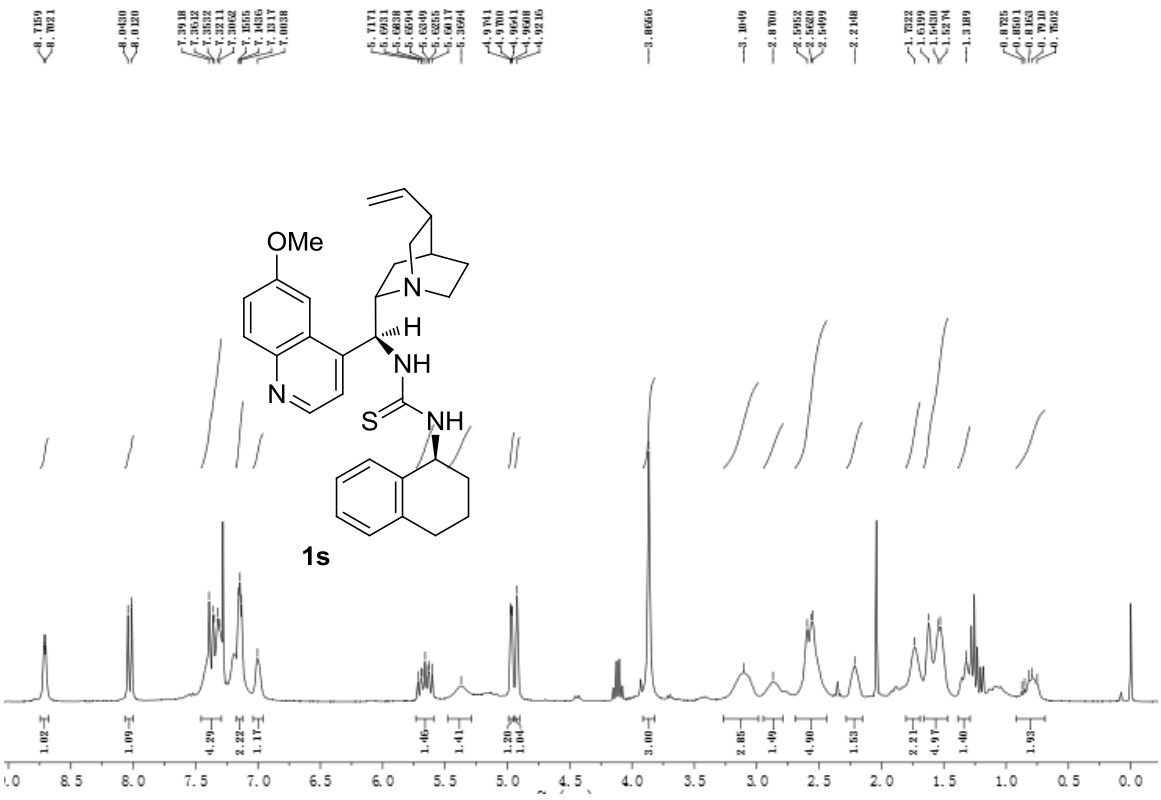
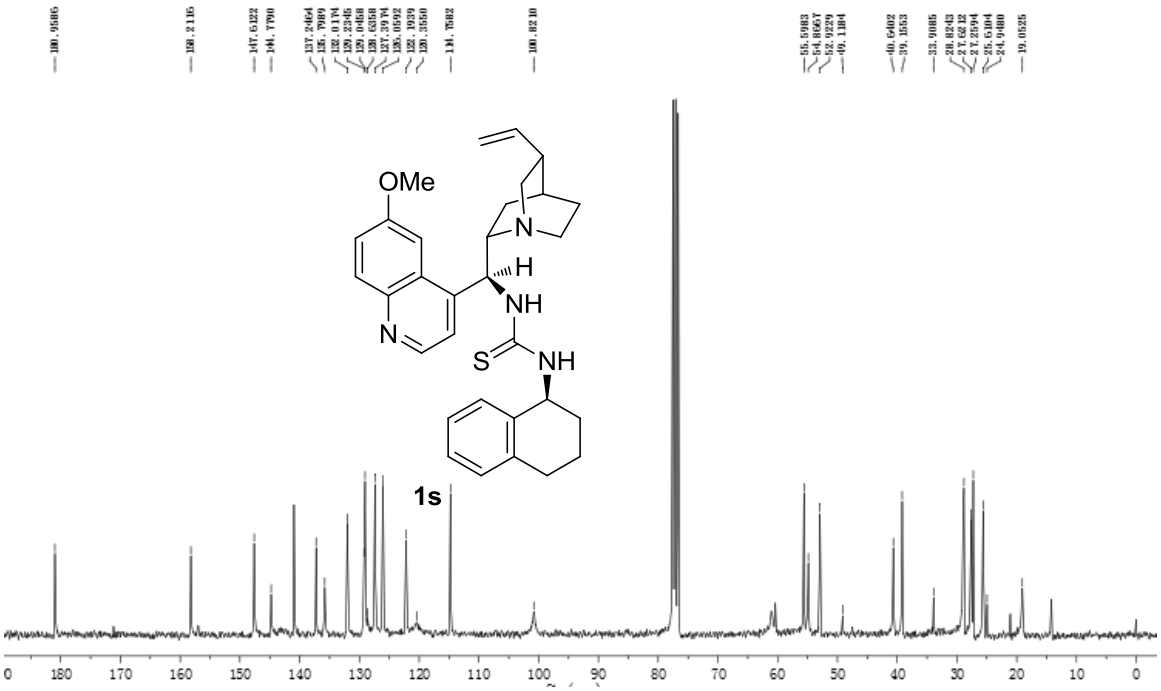
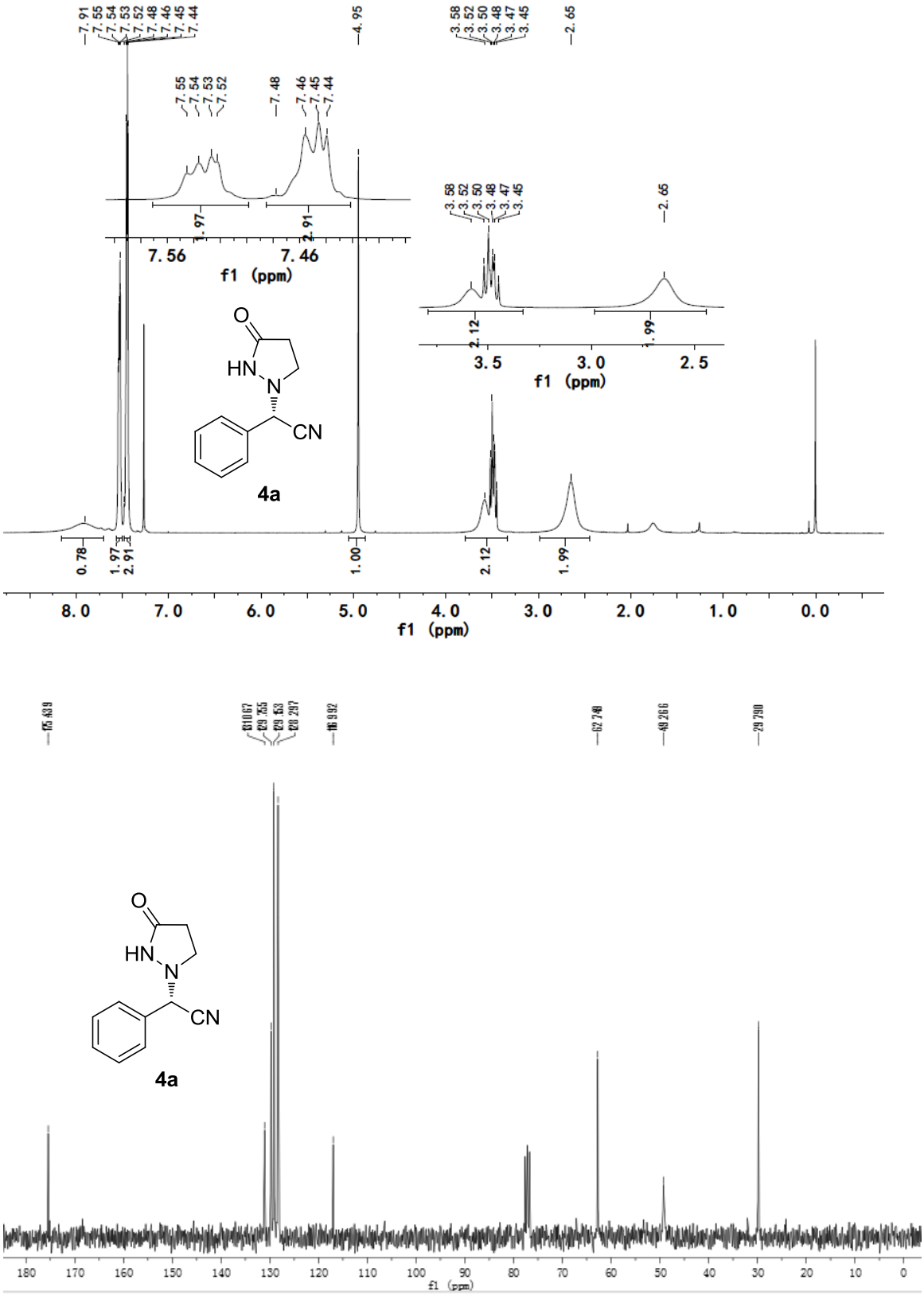
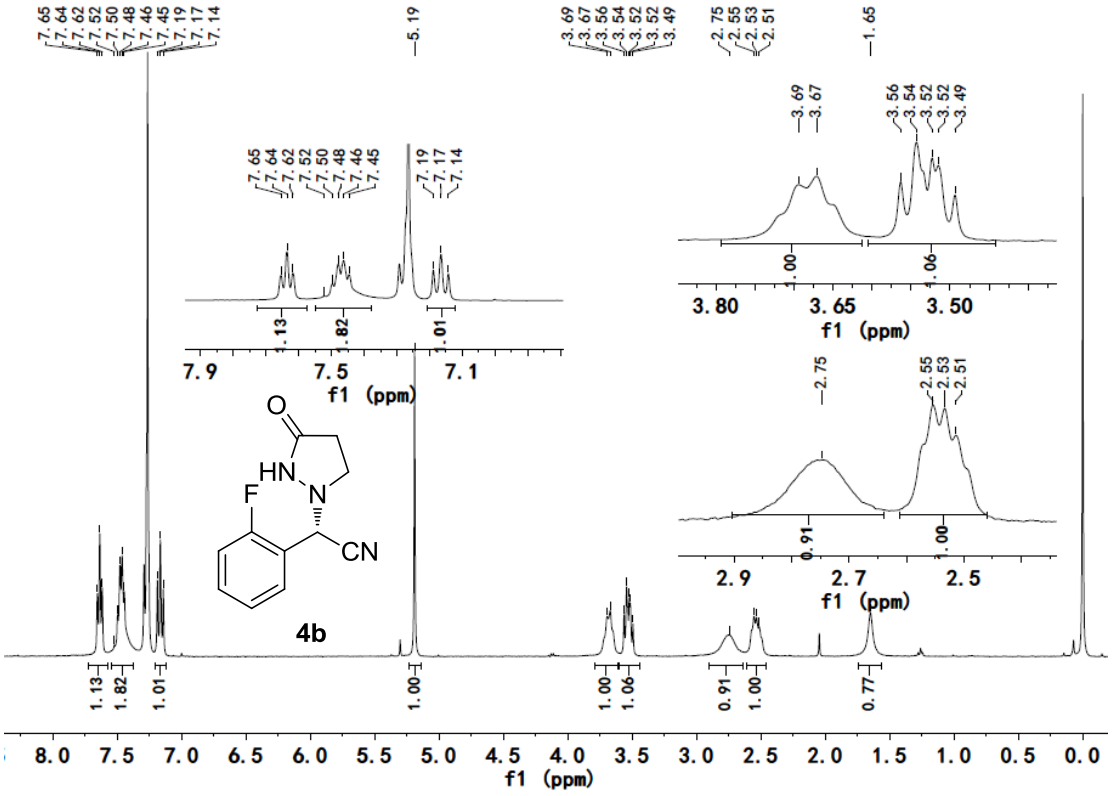


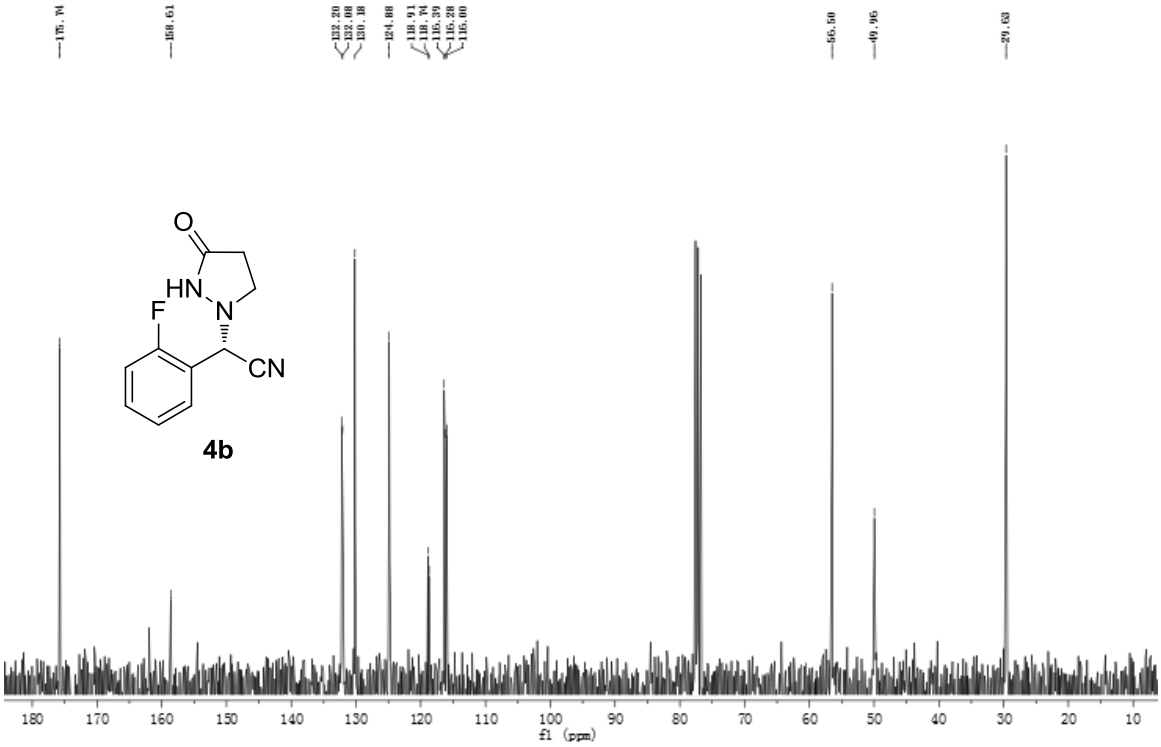


2-(3-oxopyrazolidin-1-yl)-2-phenylacetonitrile 4a

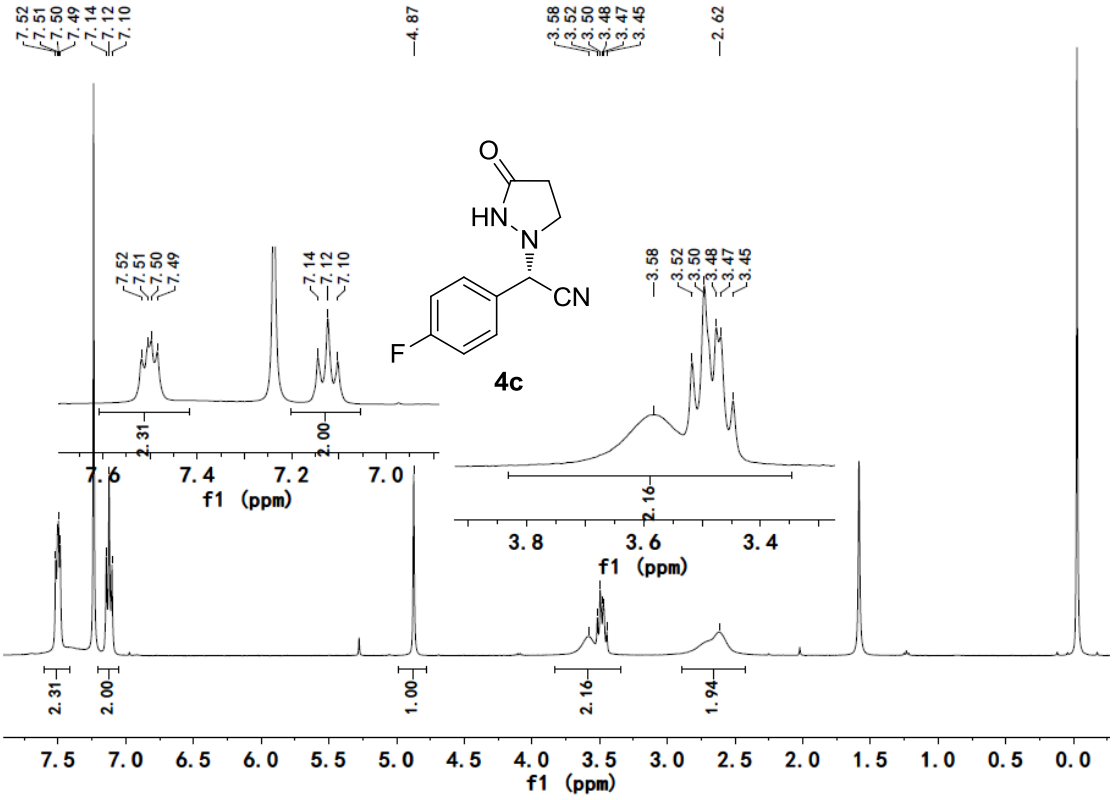


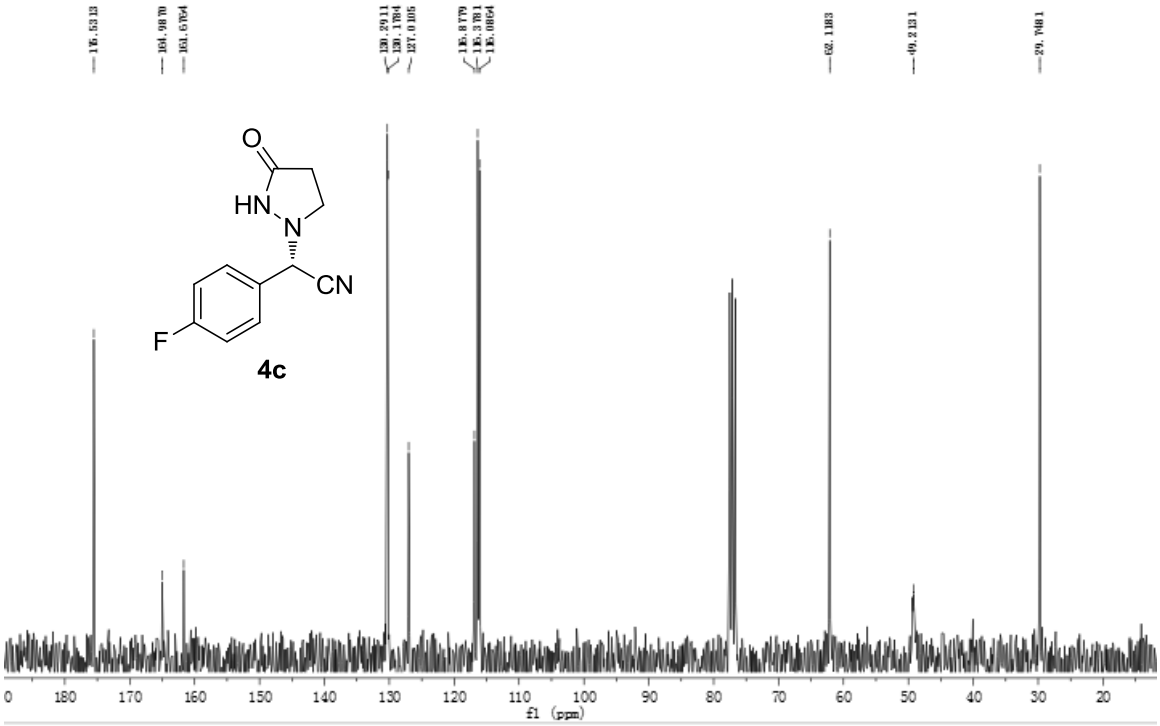
2-(2-fluorophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4b



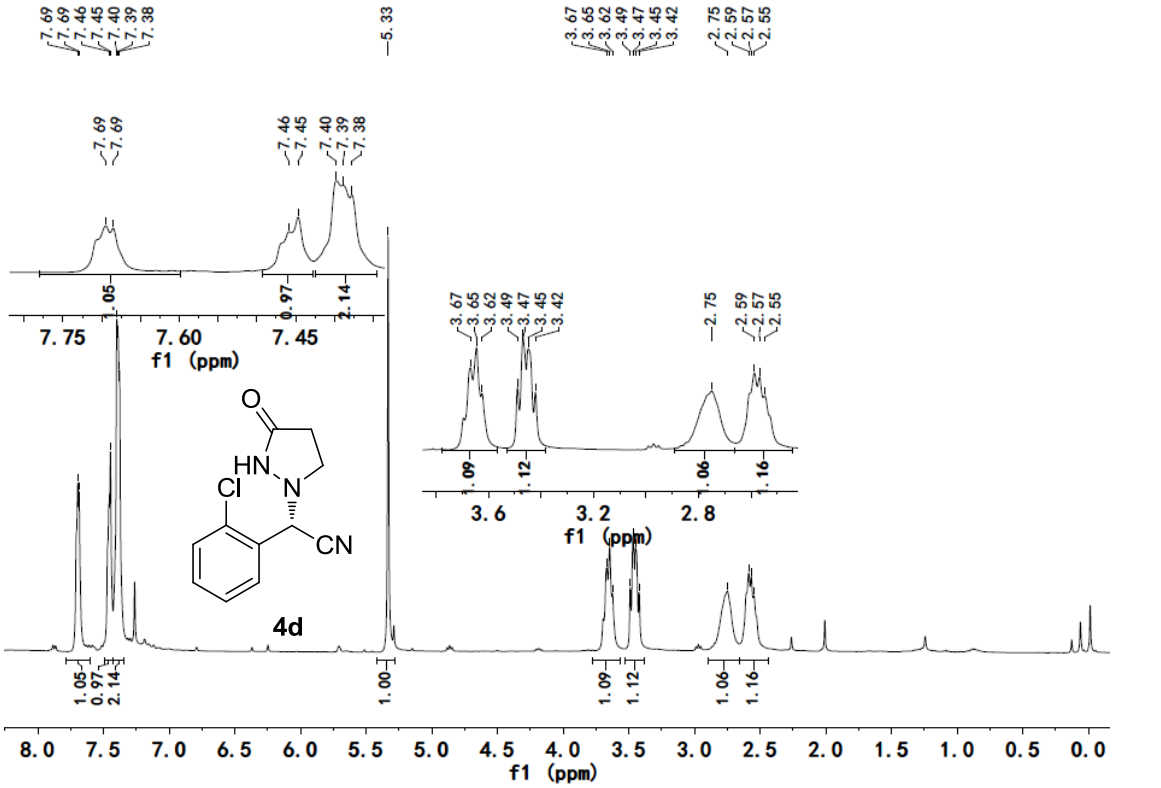


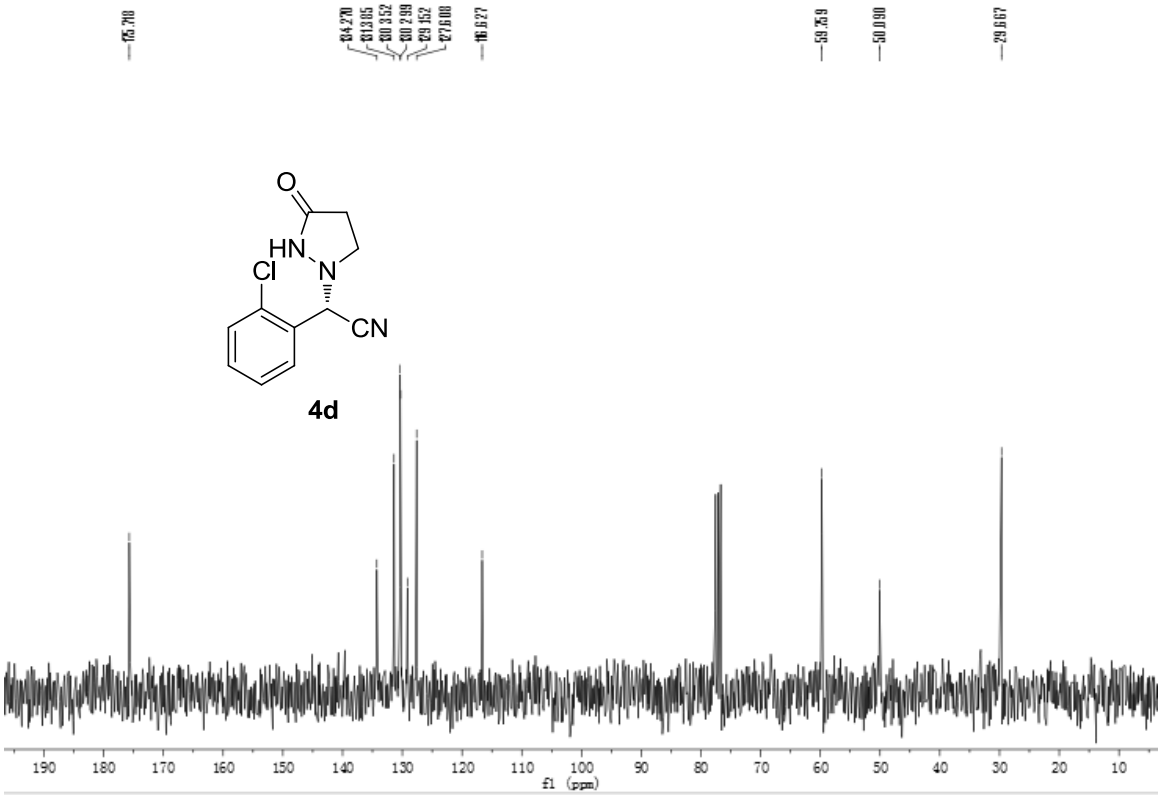
2-(4-fluorophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4c



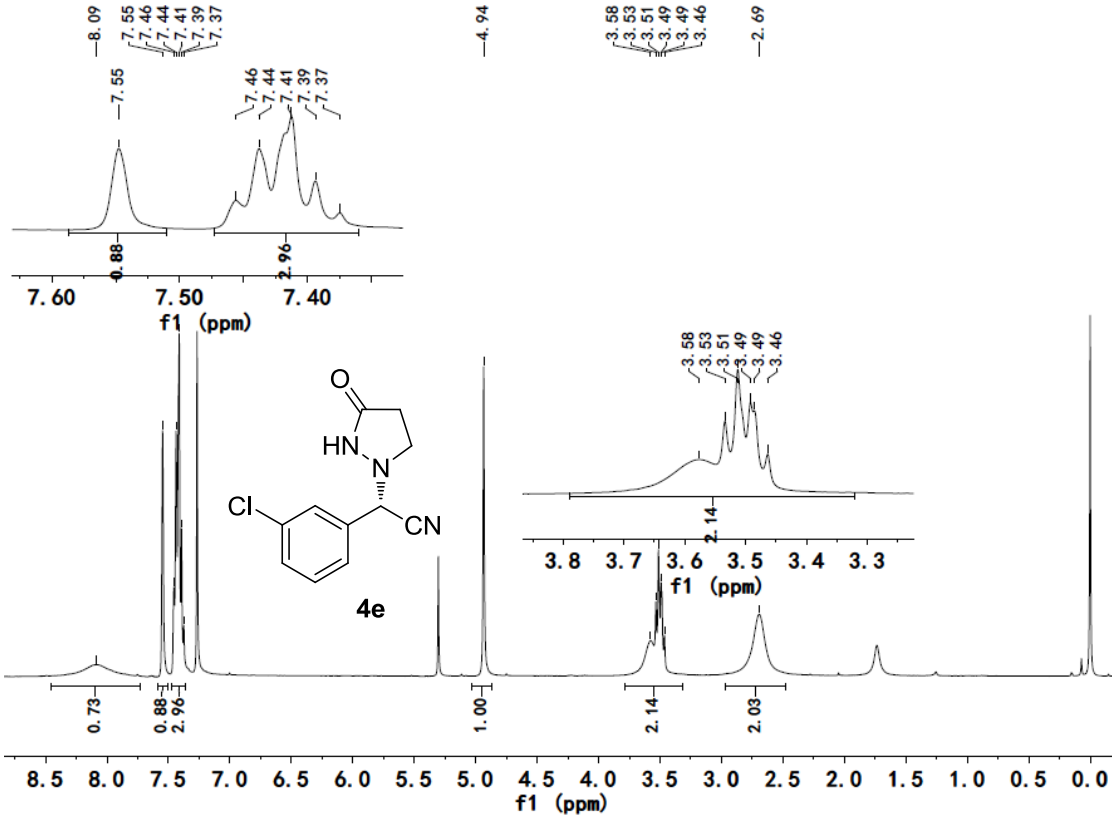


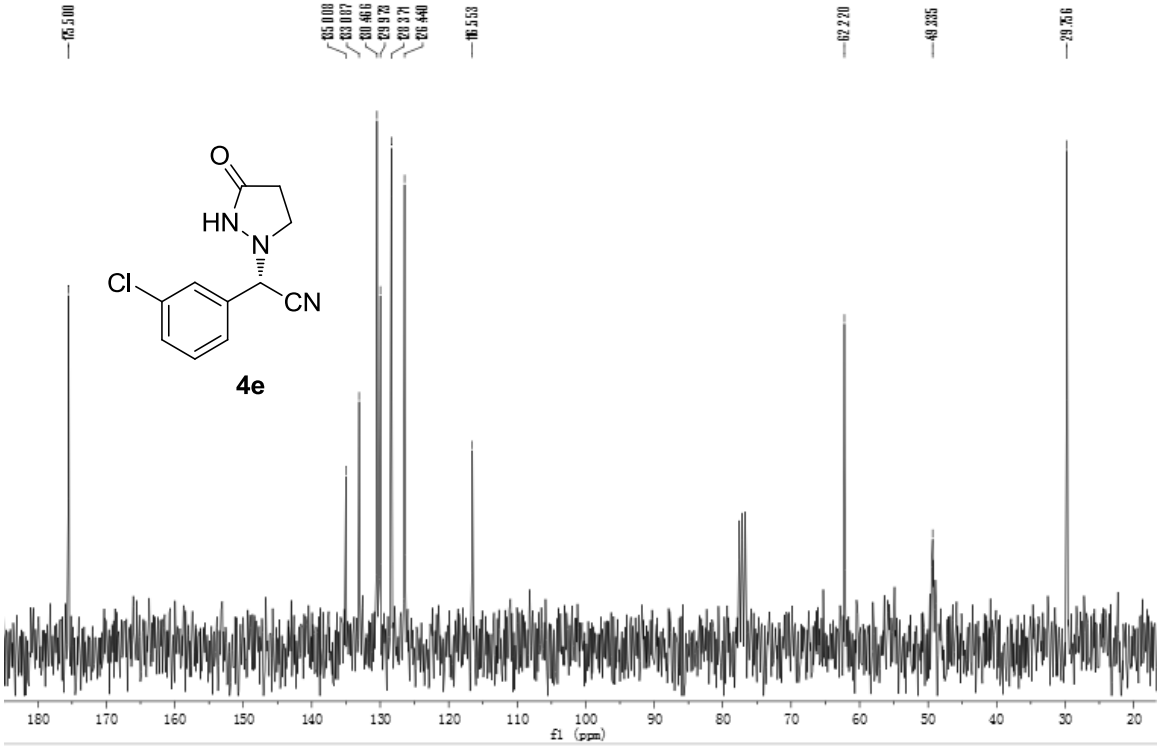
2-(2-chlorophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4d



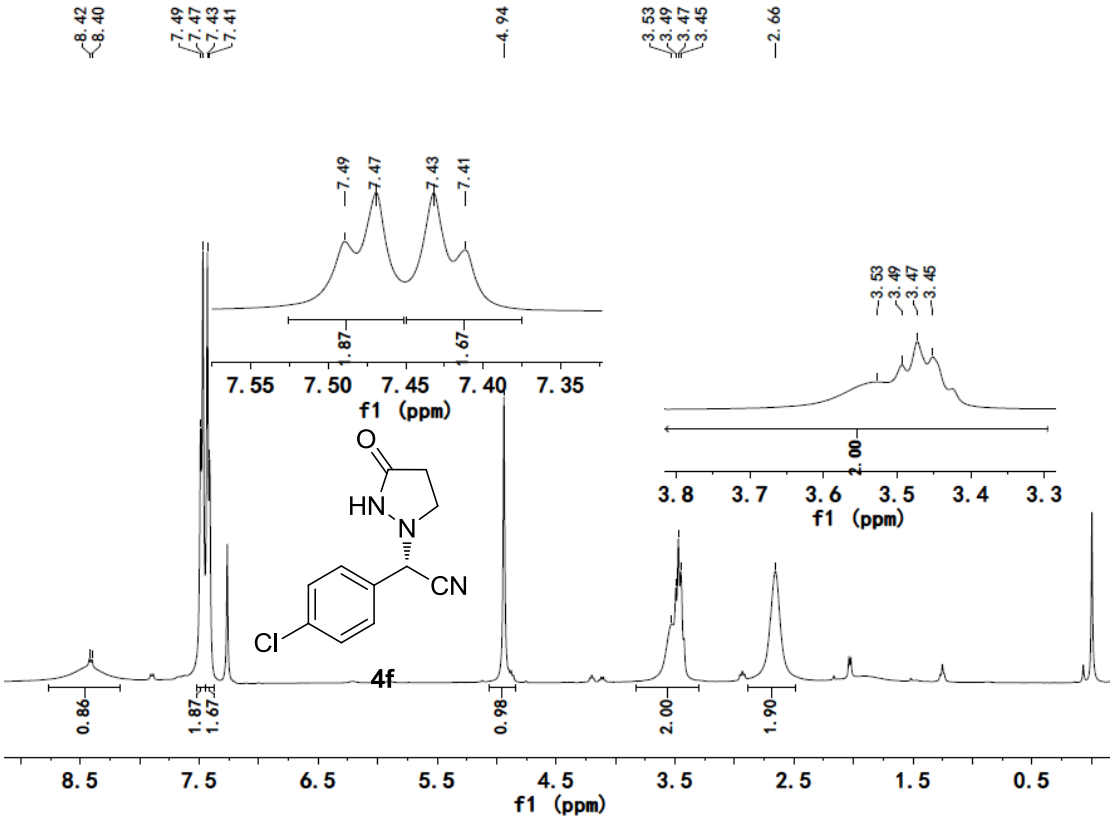


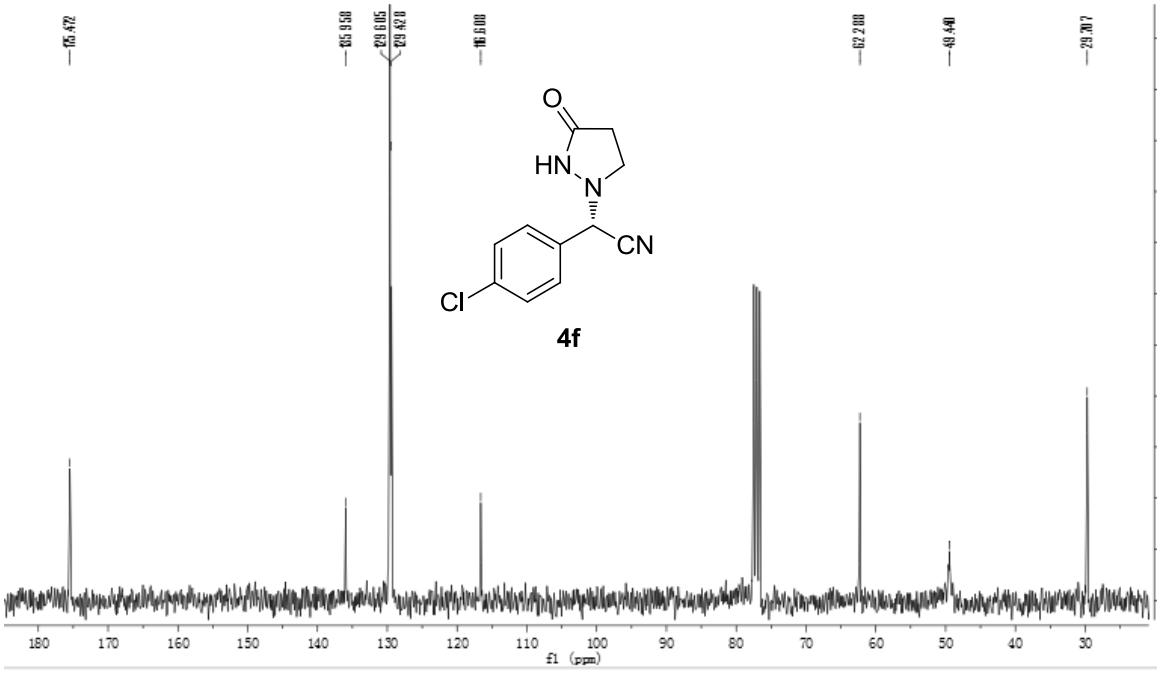
2-(3-chlorophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4e



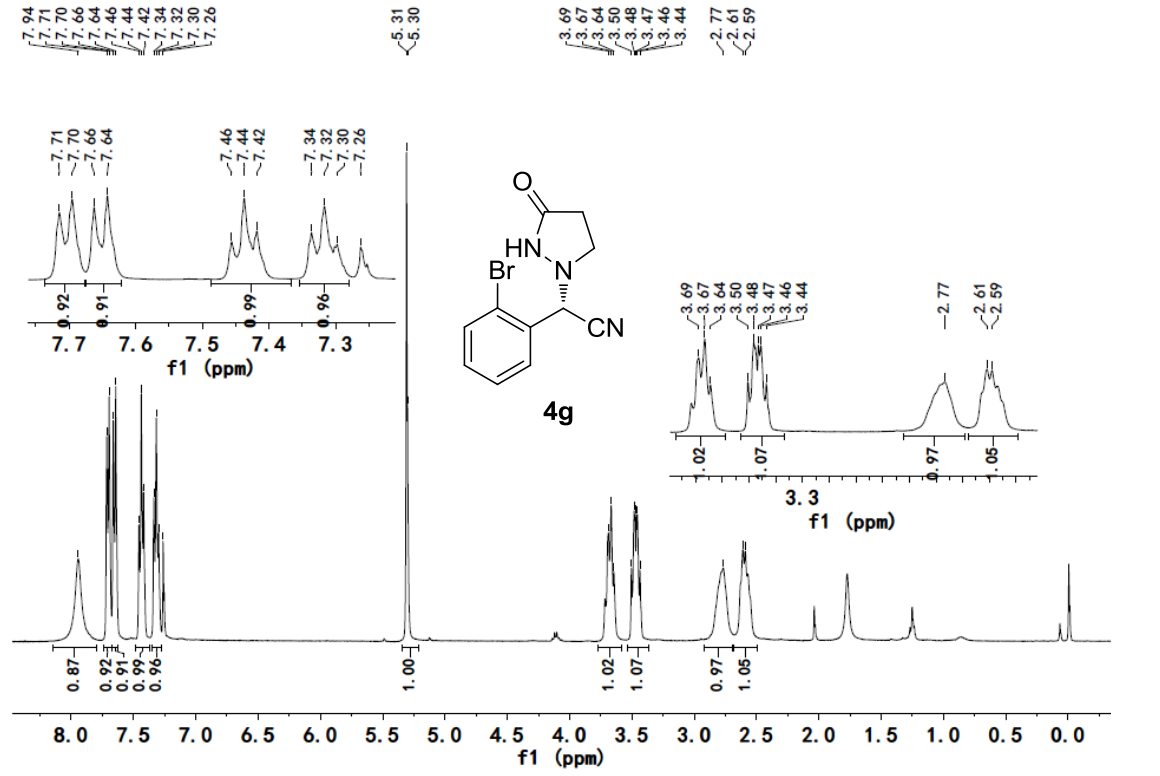


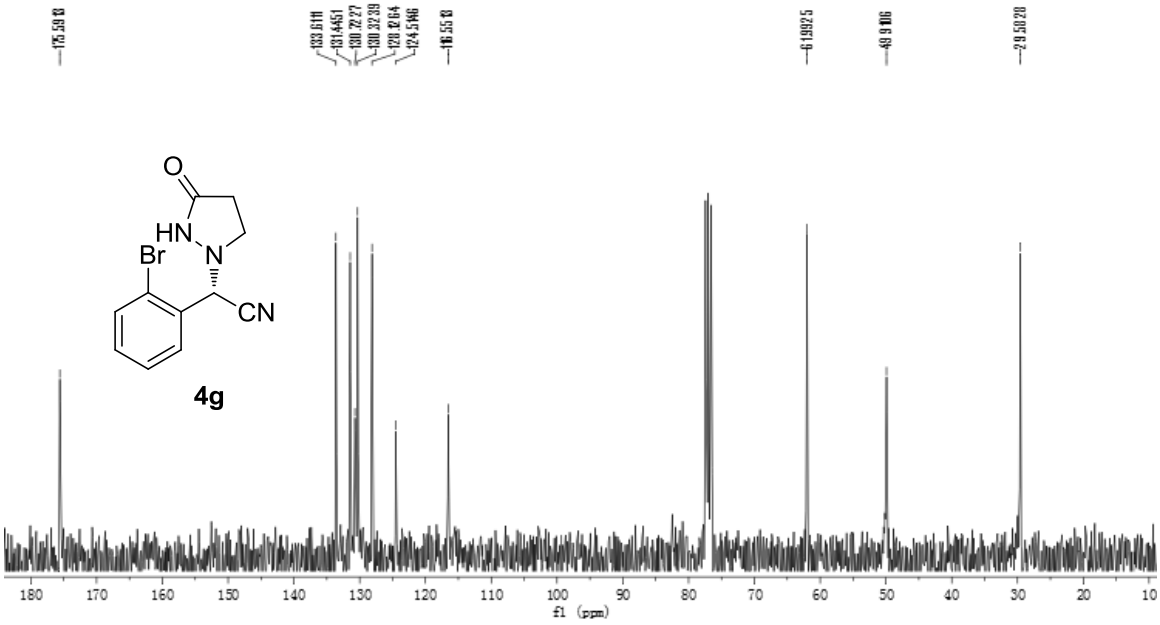
2-(4-chlorophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4f



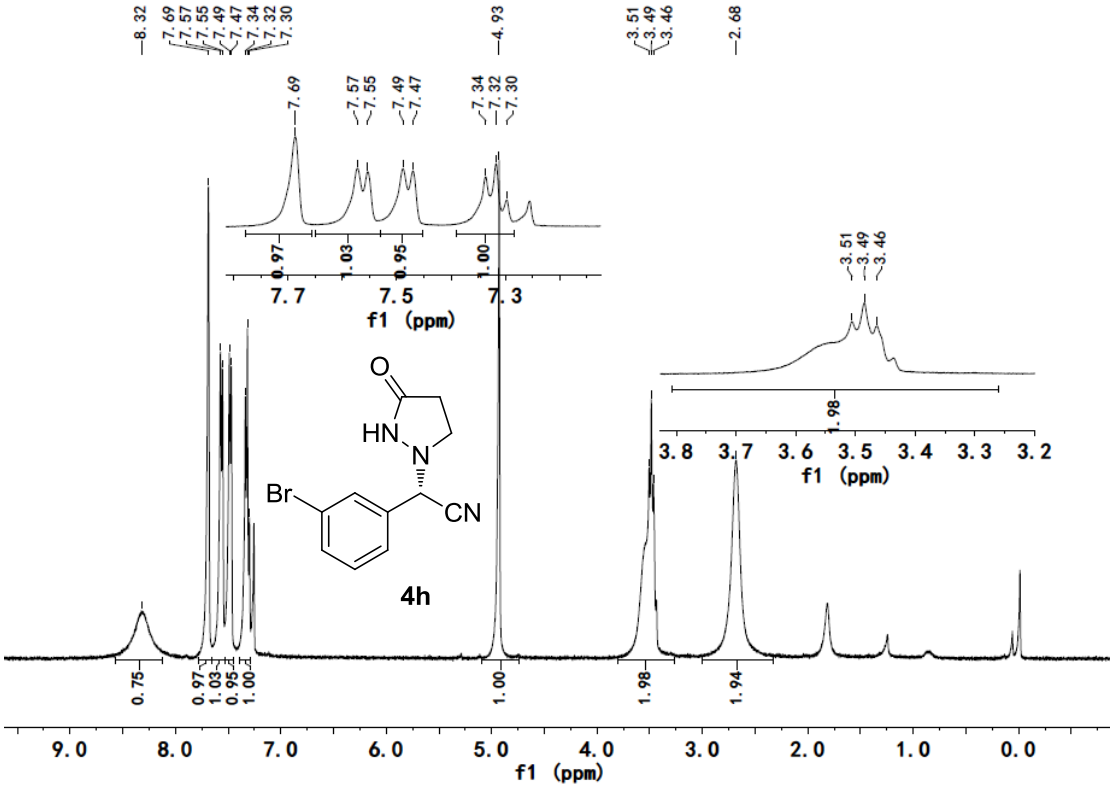


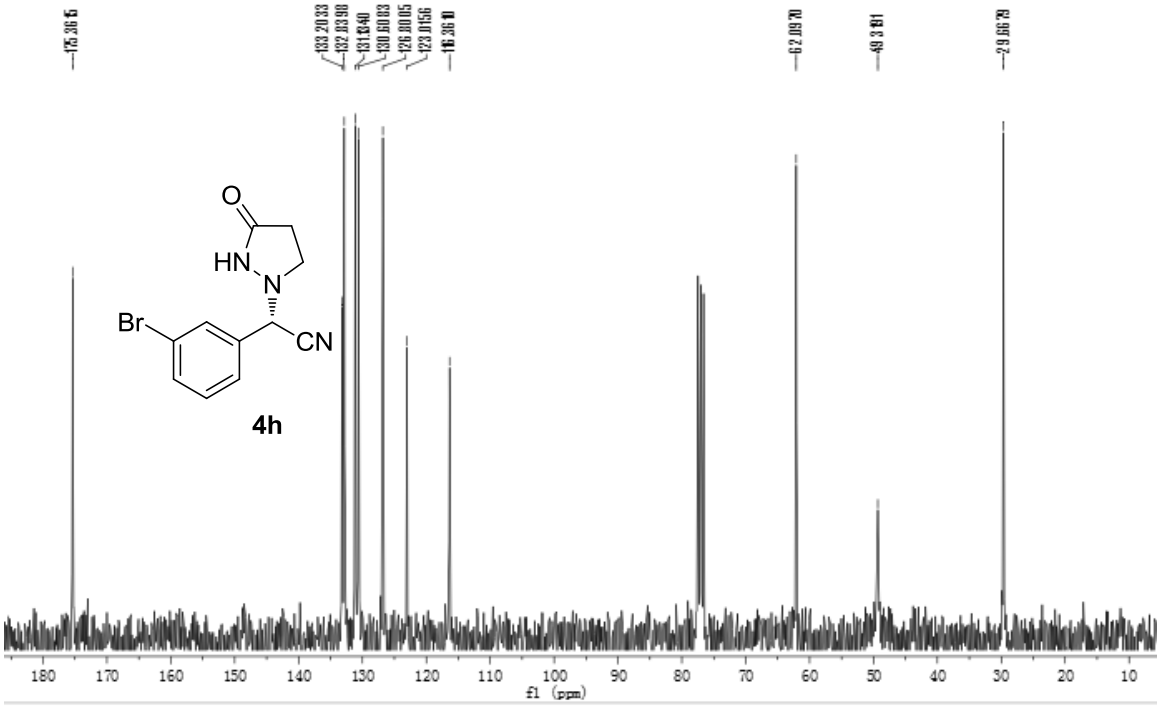
2-(2-bromophenyl)-2-(3-oxopyrazolidin-1-yl)acetonitrile 4g



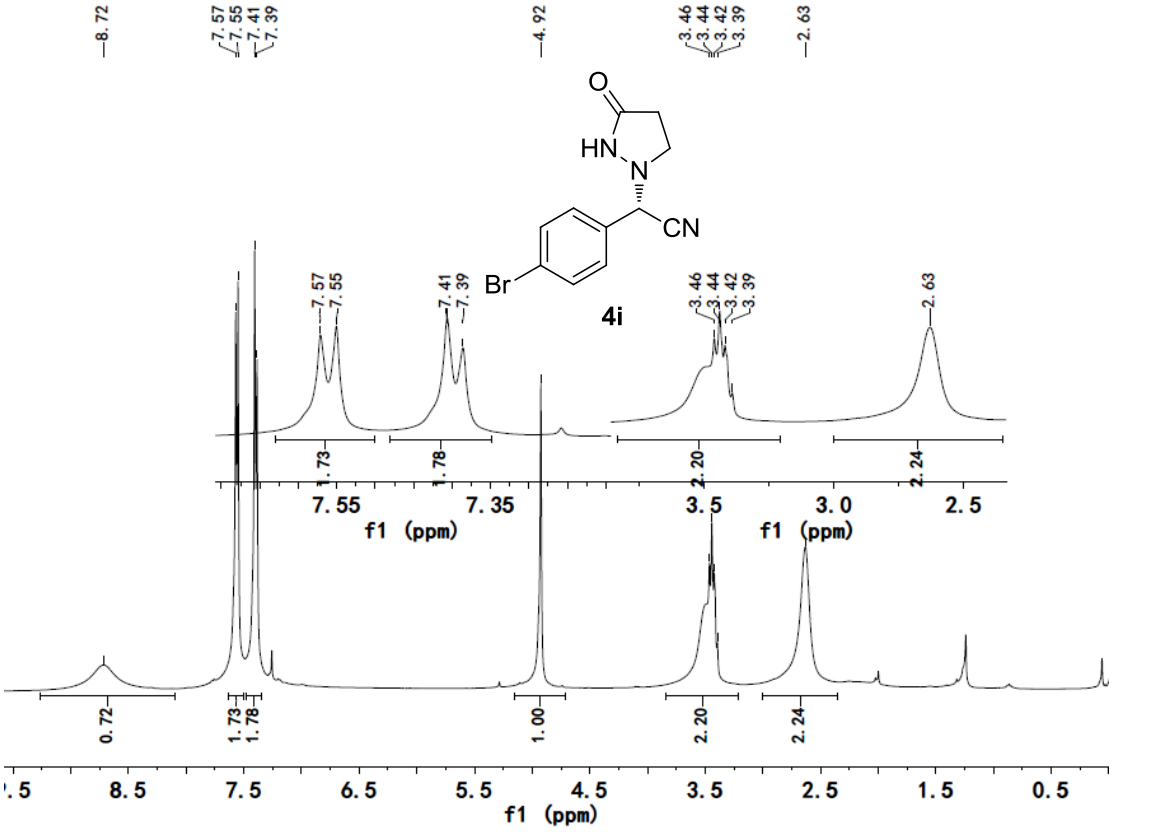


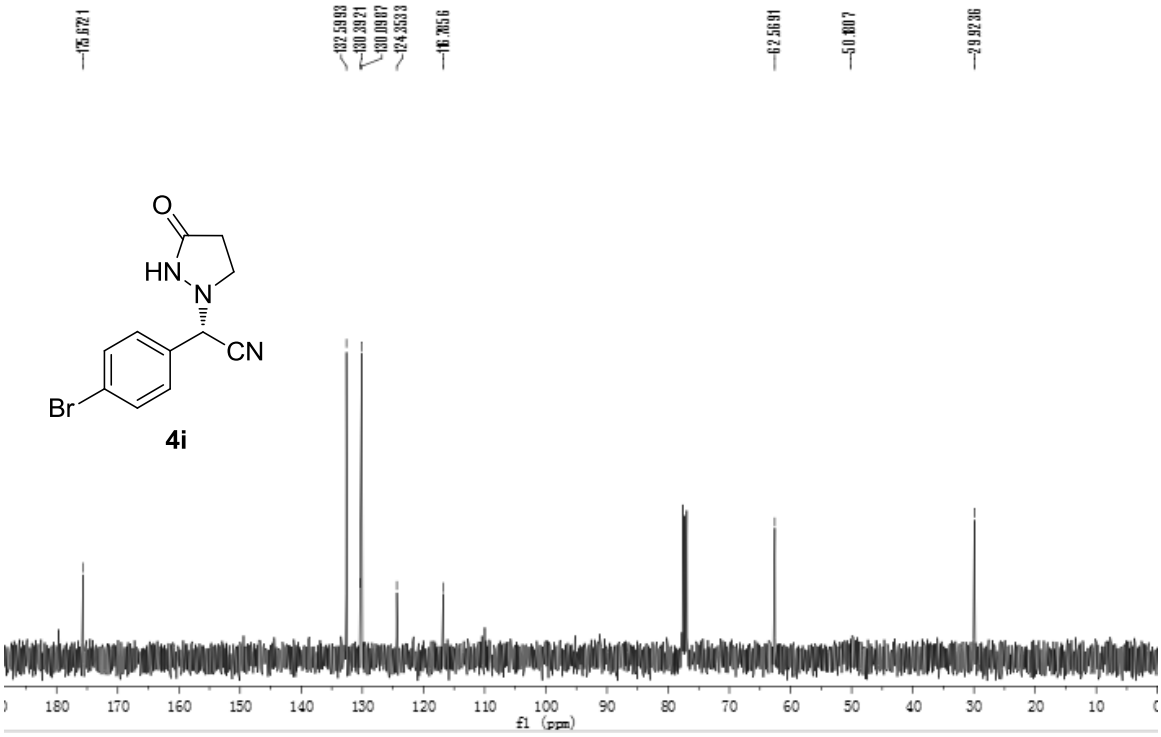
2-(3-bromophenyl)-2-(3-oxopyrazolidin-1-yl)acetonitrile 4h



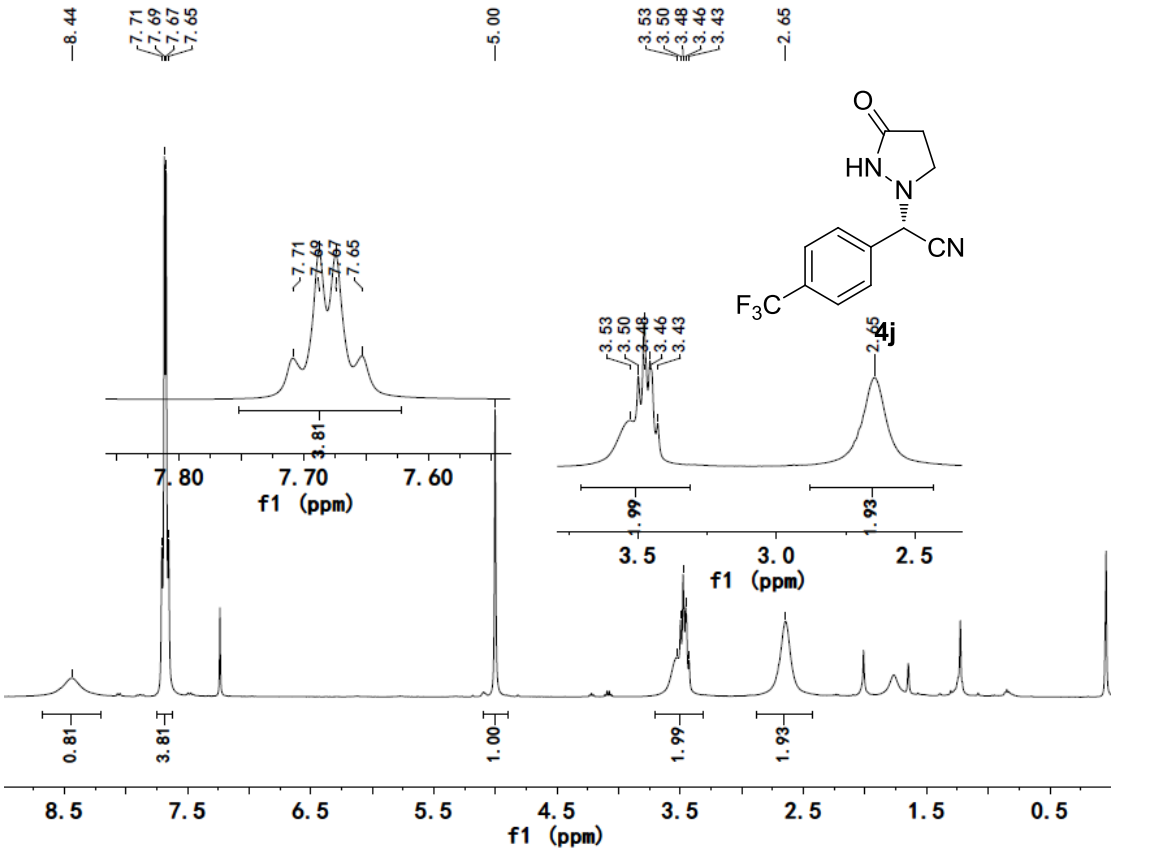


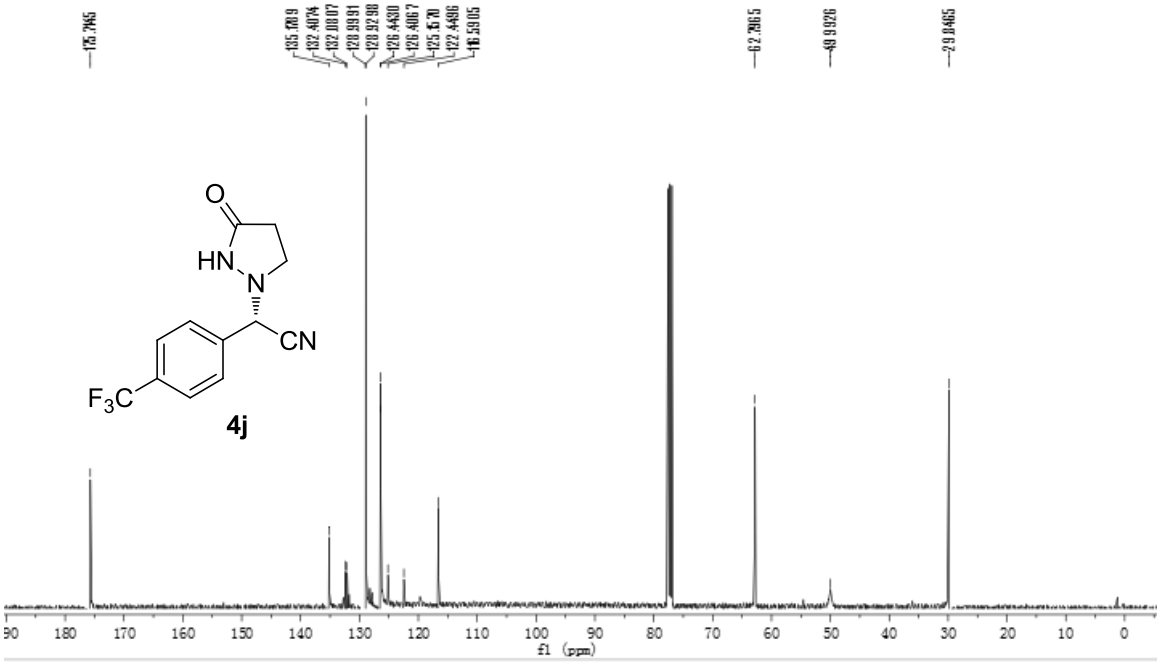
2-(4-bromophenyl)-2-(3-oxopyrazolidin-1-yl)acetonitrile 4i



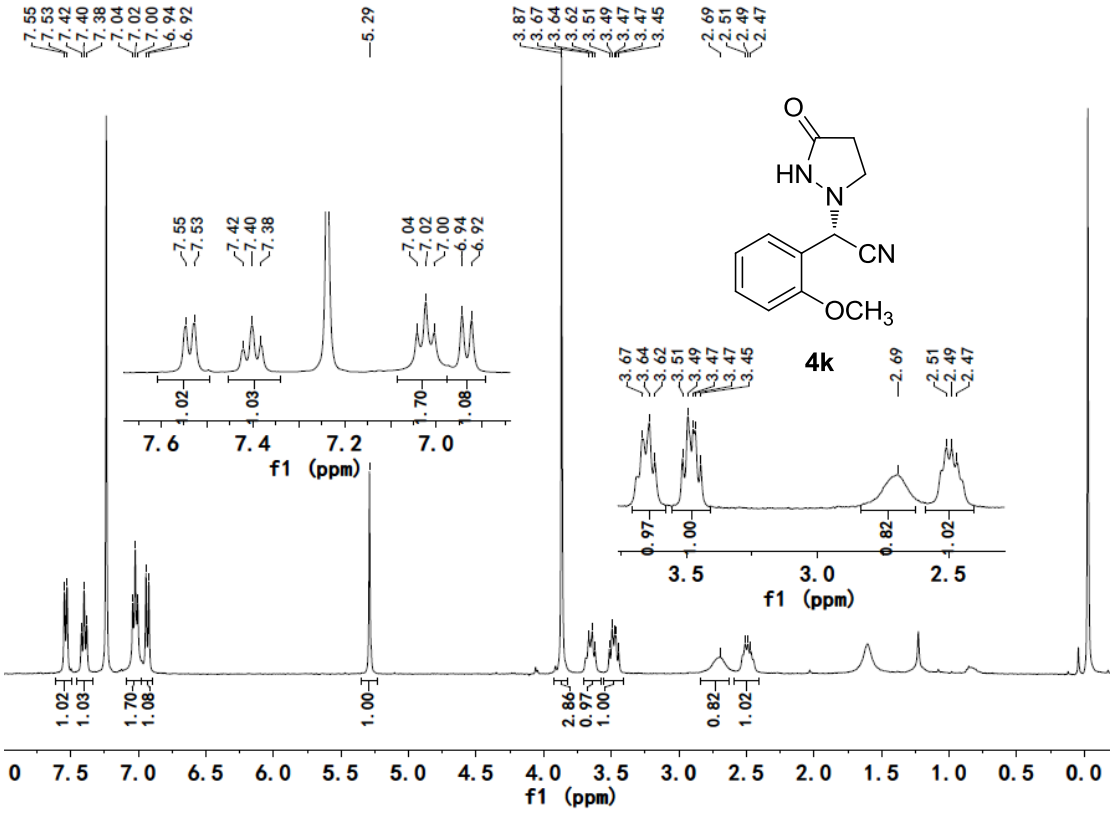


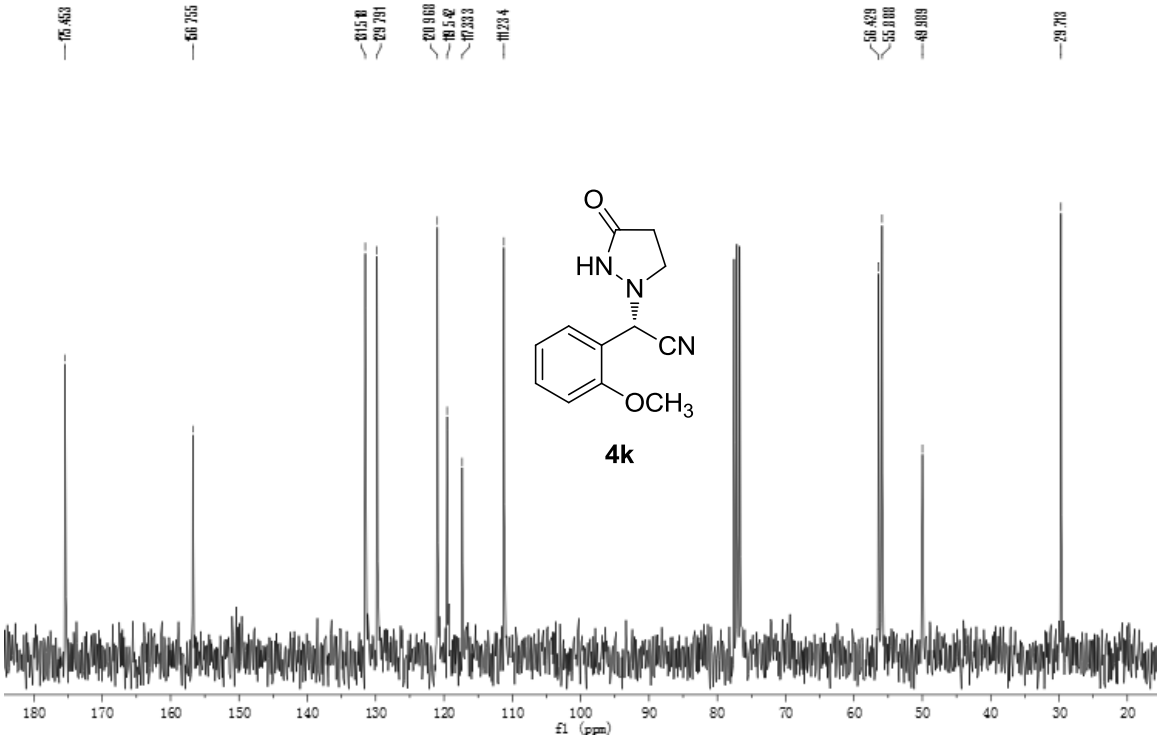
2-(3-oxopyrazolidin-1-yl)-2-(4-(trifluoromethyl)phenyl)acetonitrile 4j



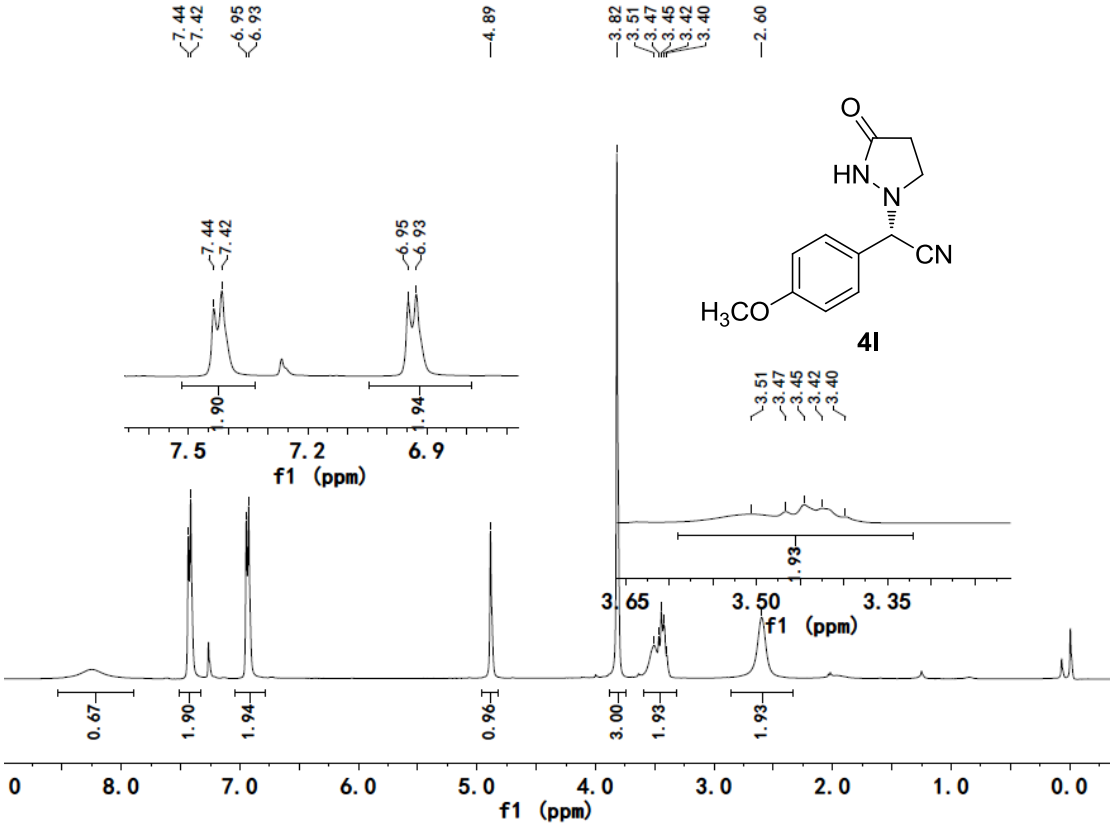


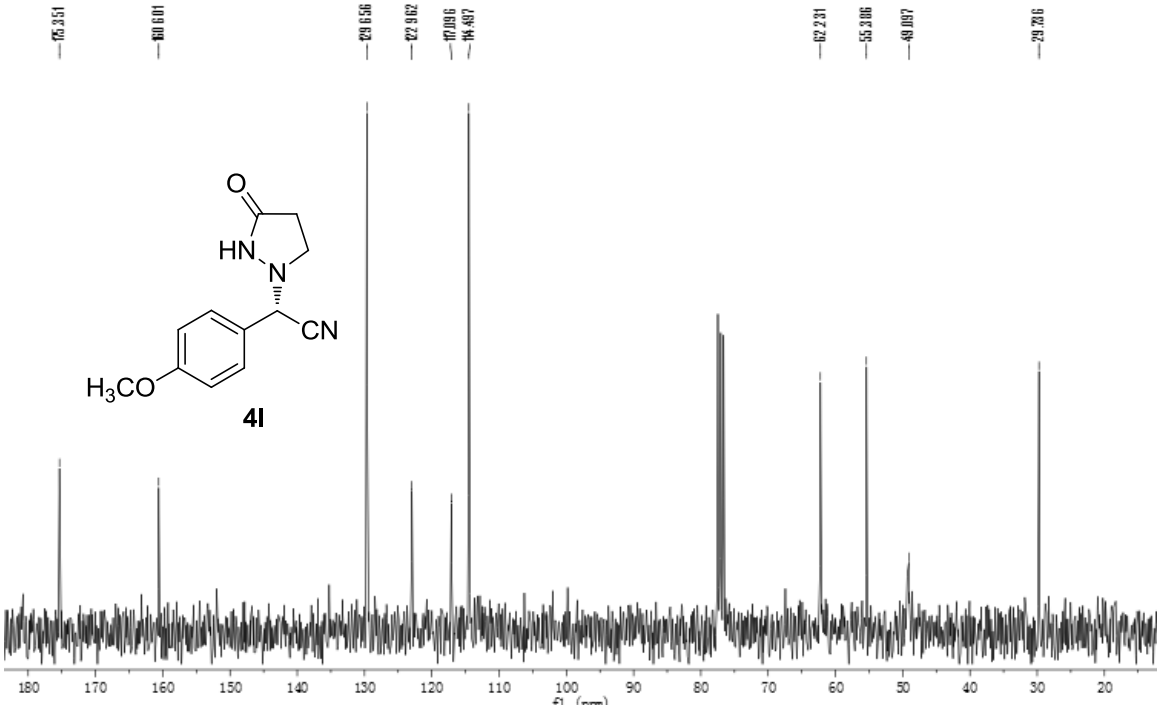
2-(2-methoxyphenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4k



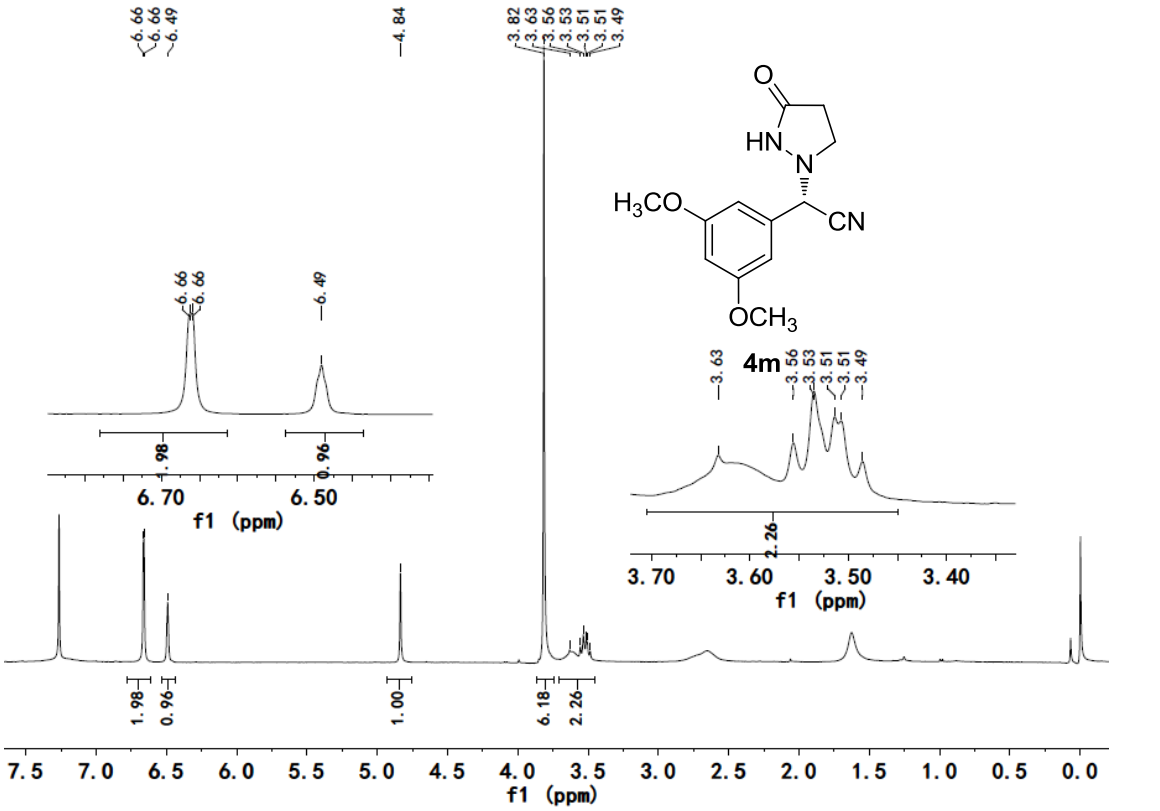


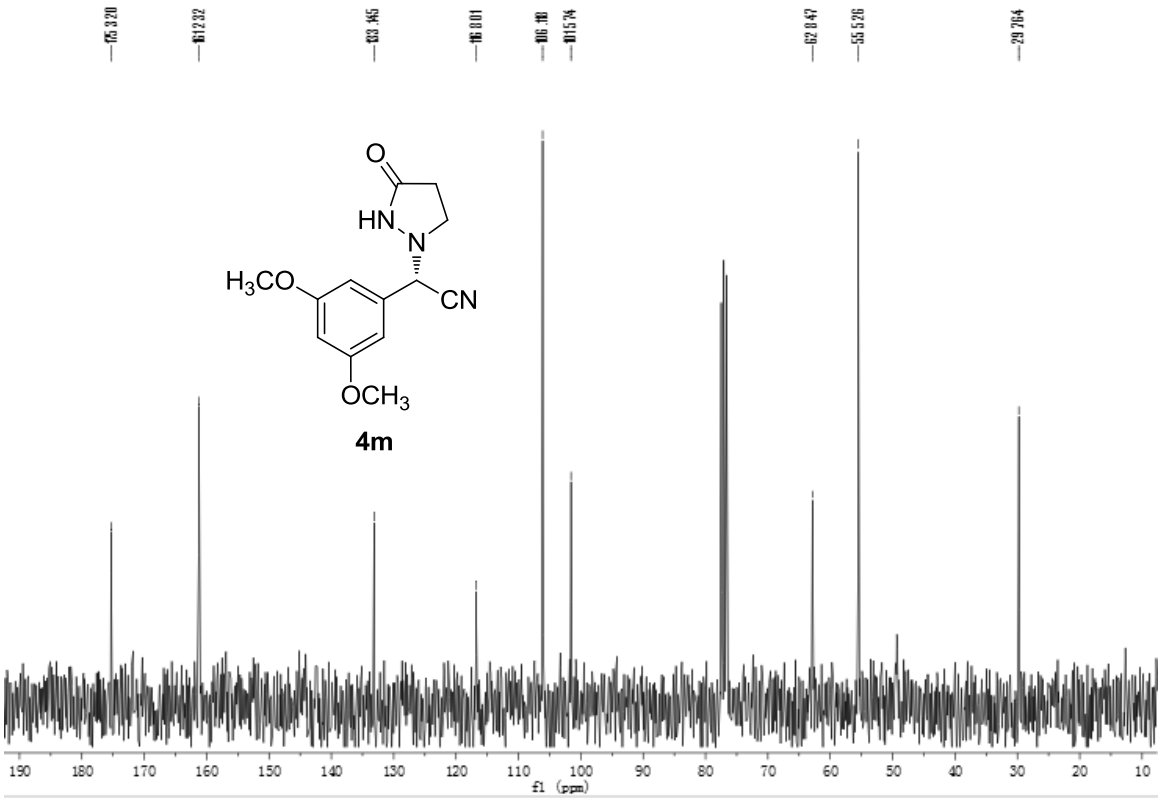
2-(4-methoxyphenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4l



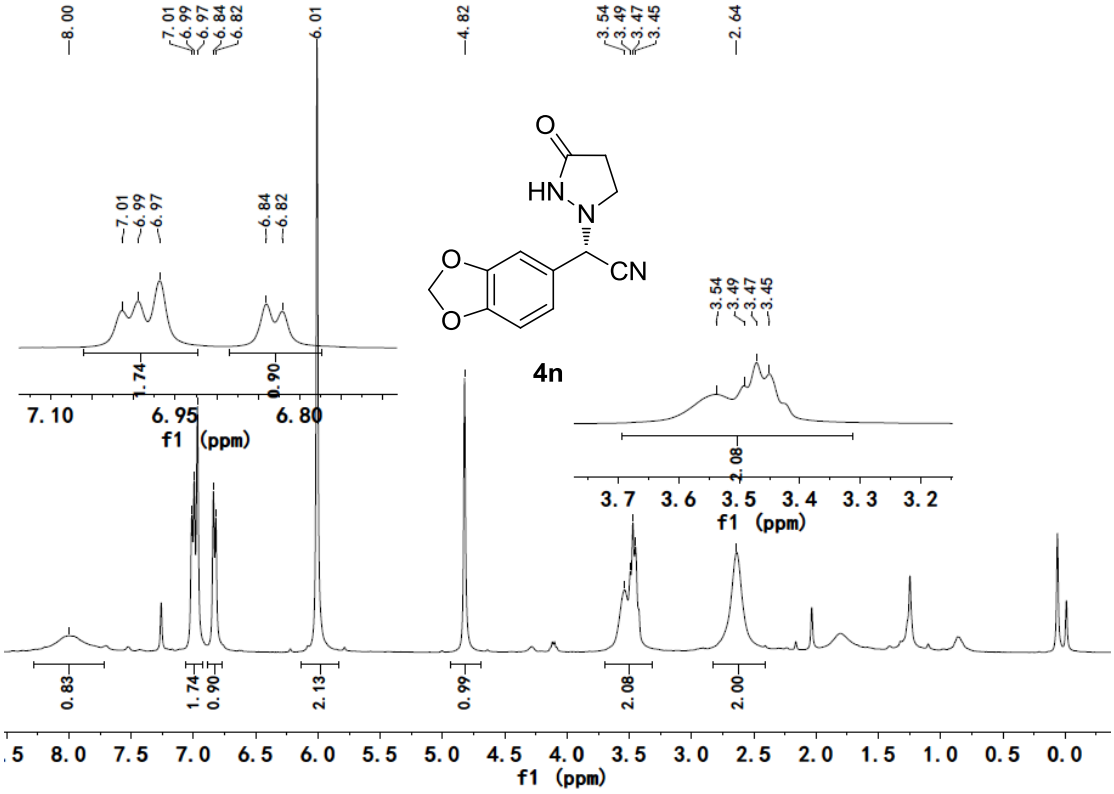


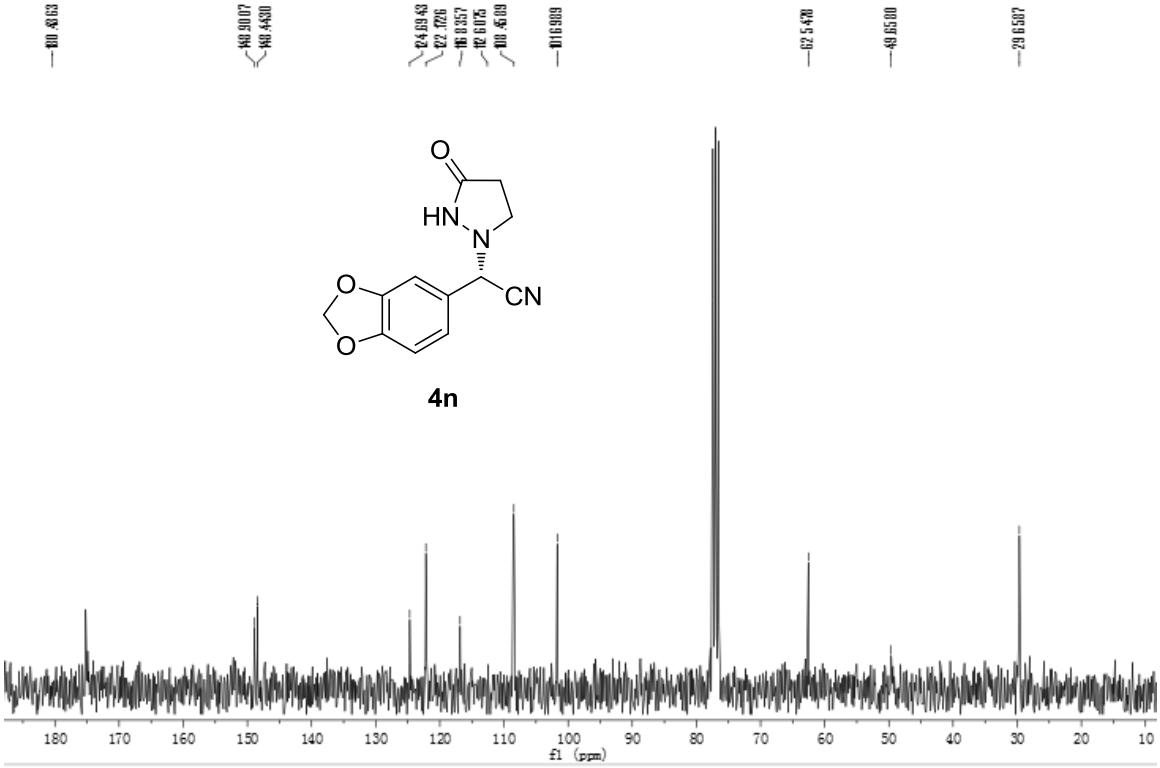
2-(3, 5-dimethoxyphenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4m



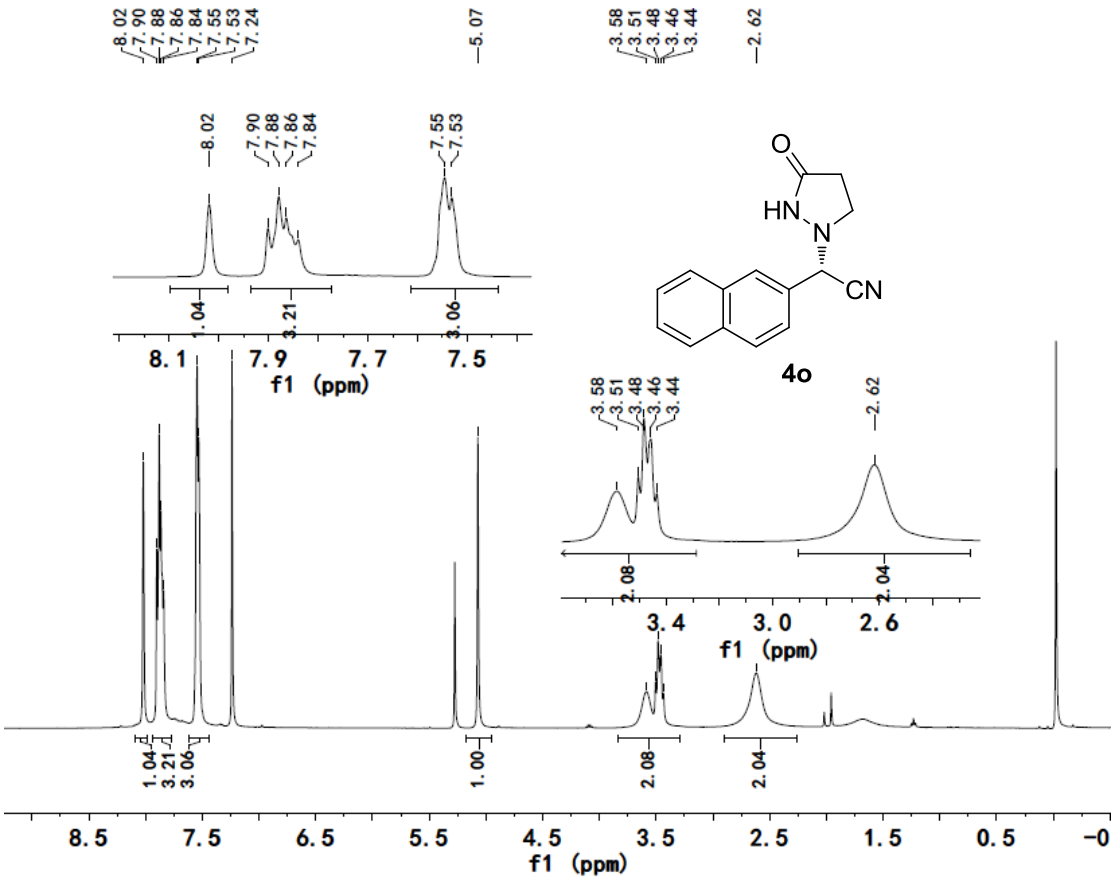


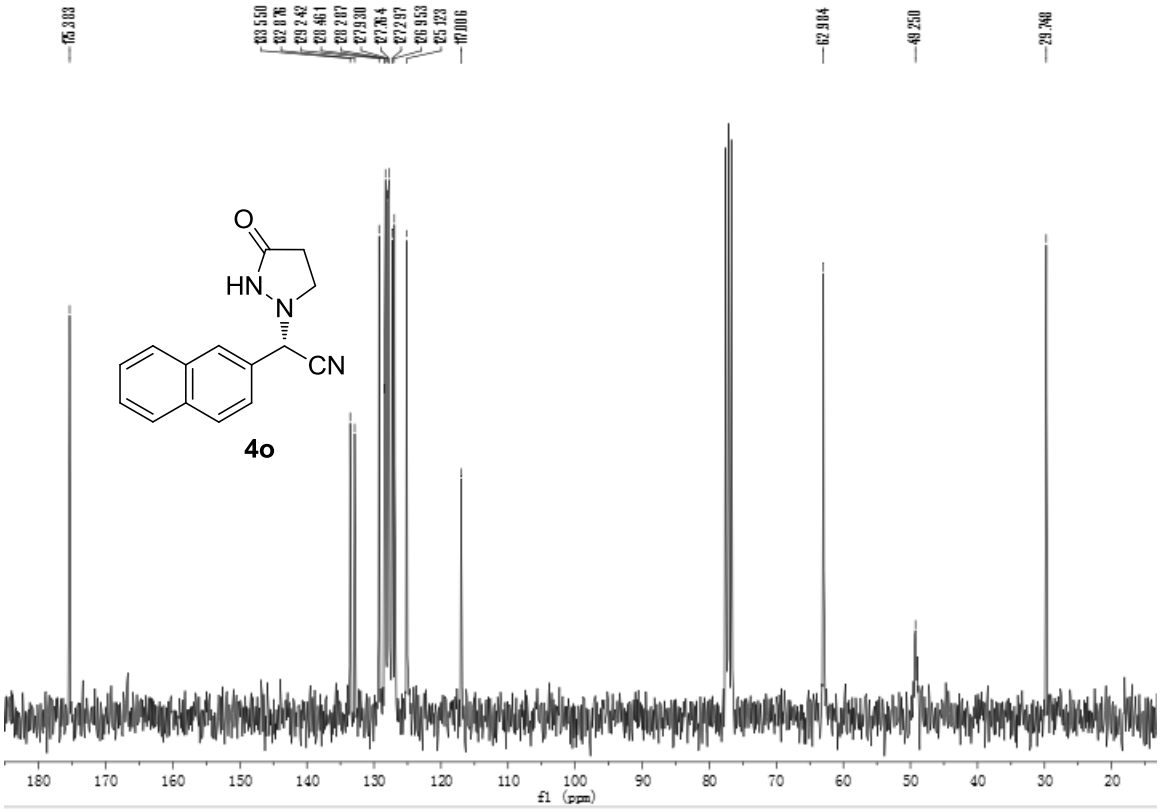
2-(benzo[d][1,3]dioxol-5-yl)-2-(3-oxopyrazolidin-1-yl)acetonitrile 4n



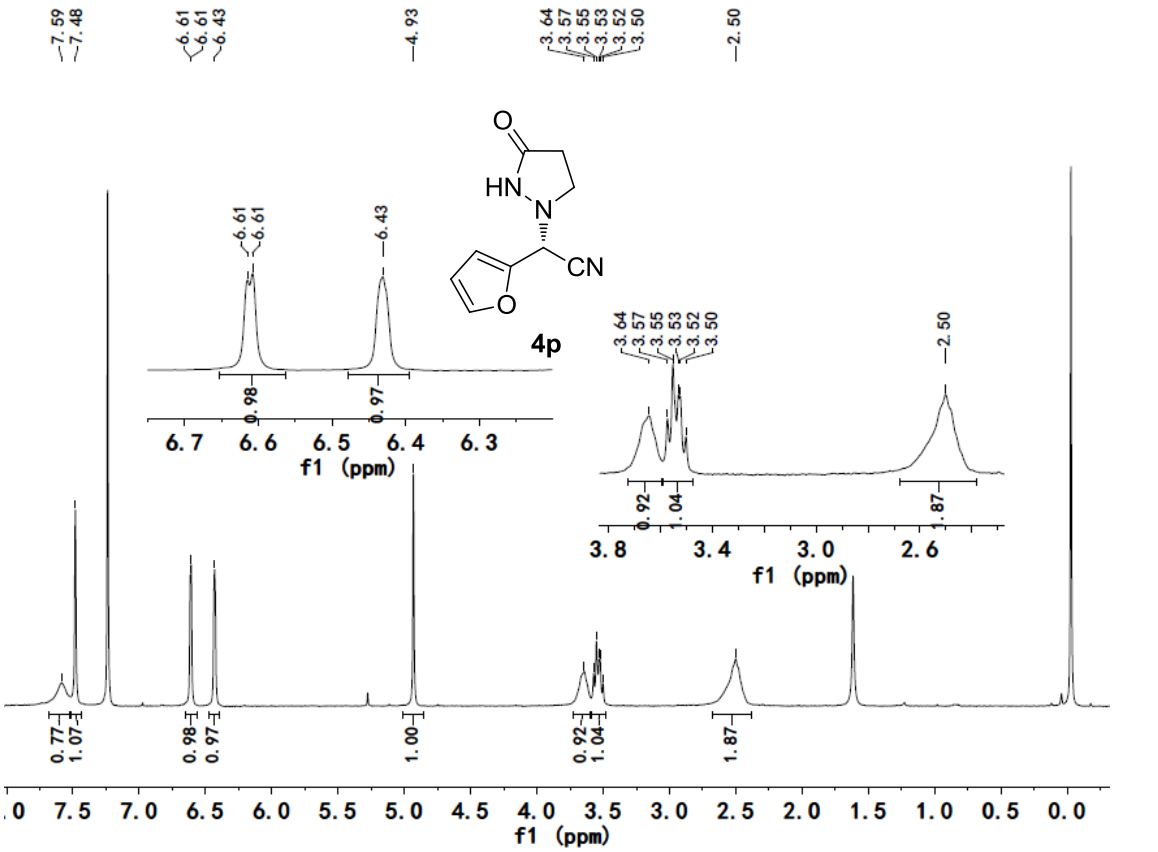


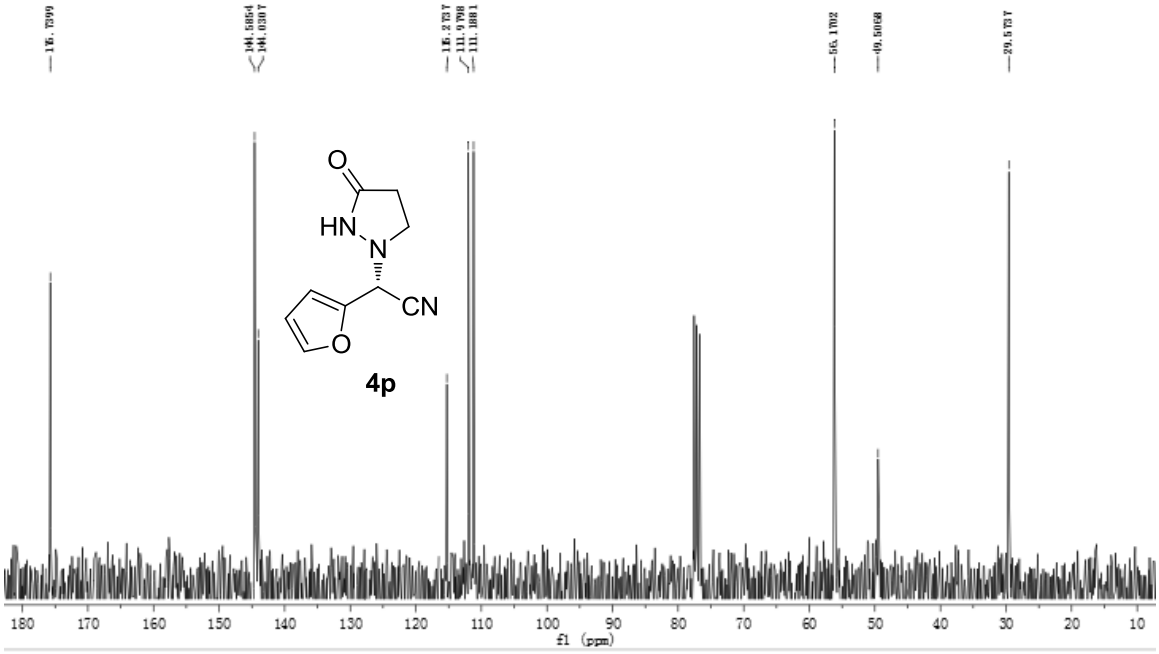
2-(naphthalen-2-yl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4o



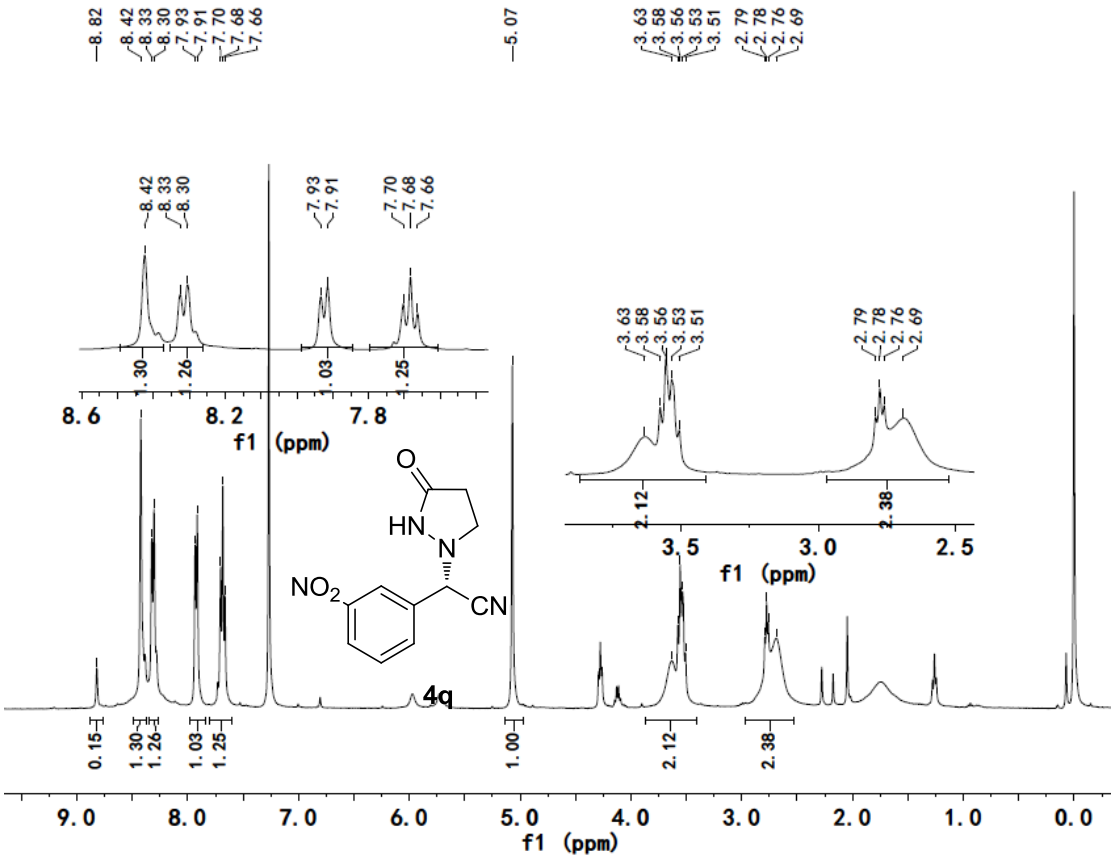


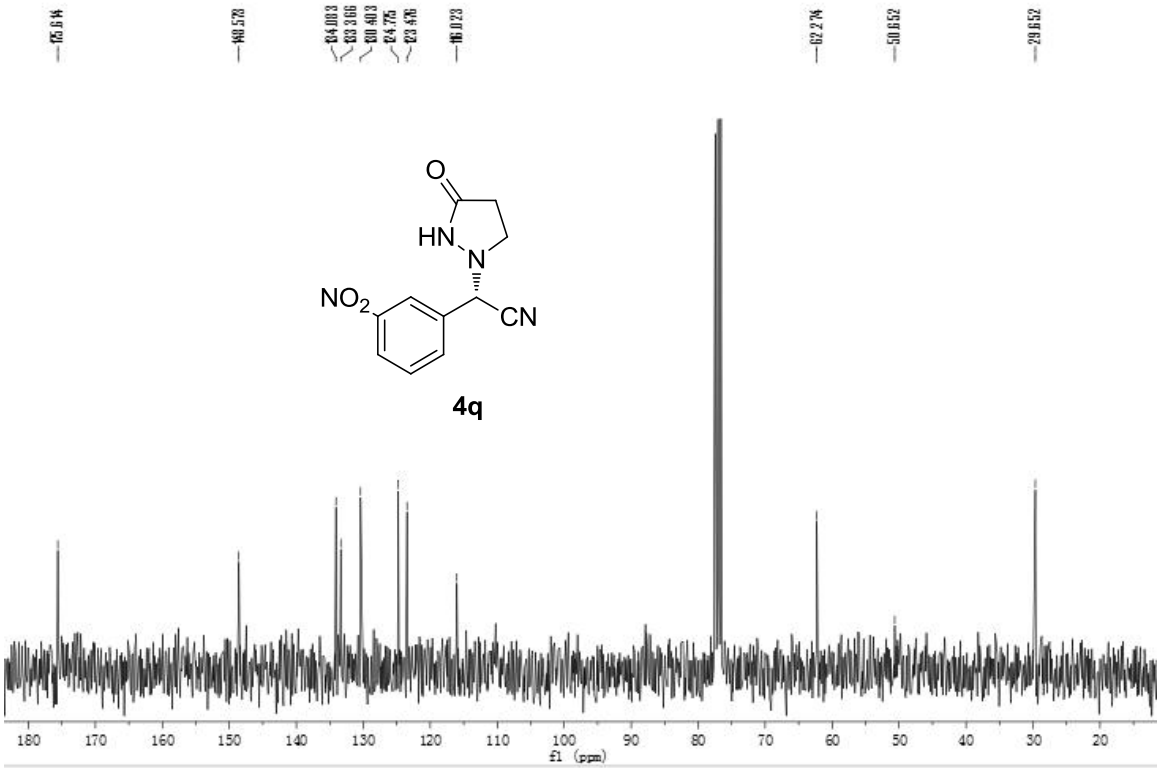
2-(furan-2-yl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4p



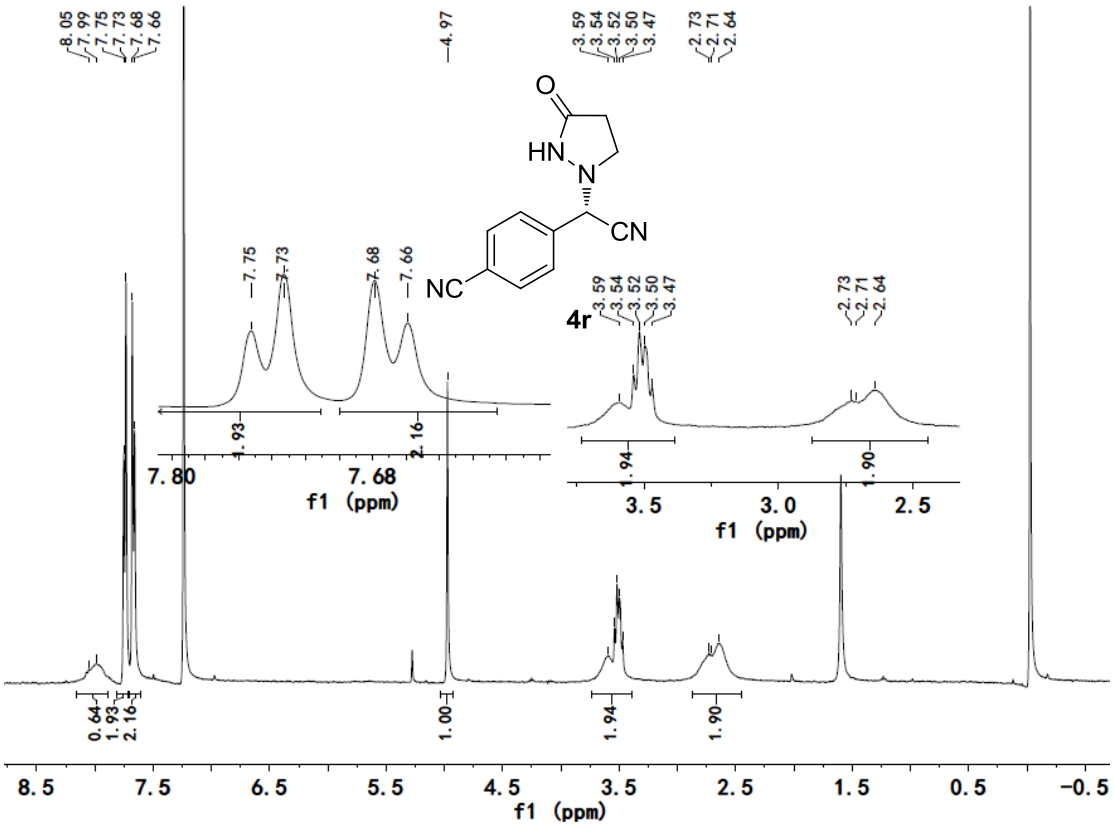


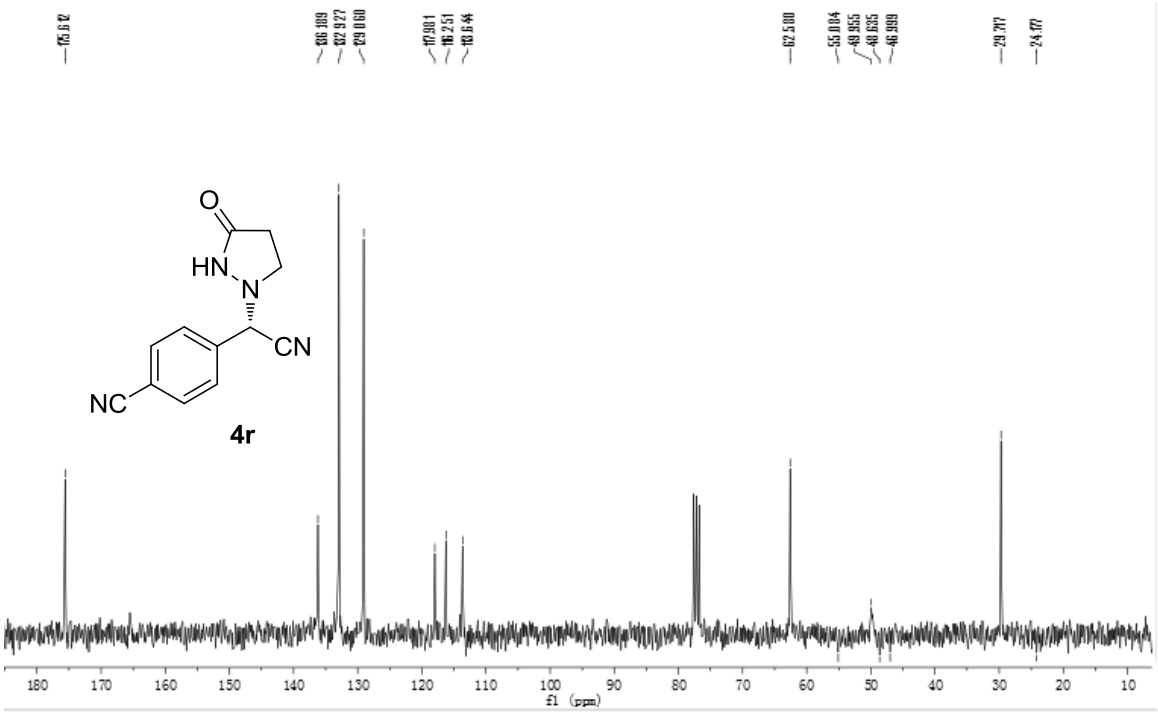
2-(3-nitrophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4q



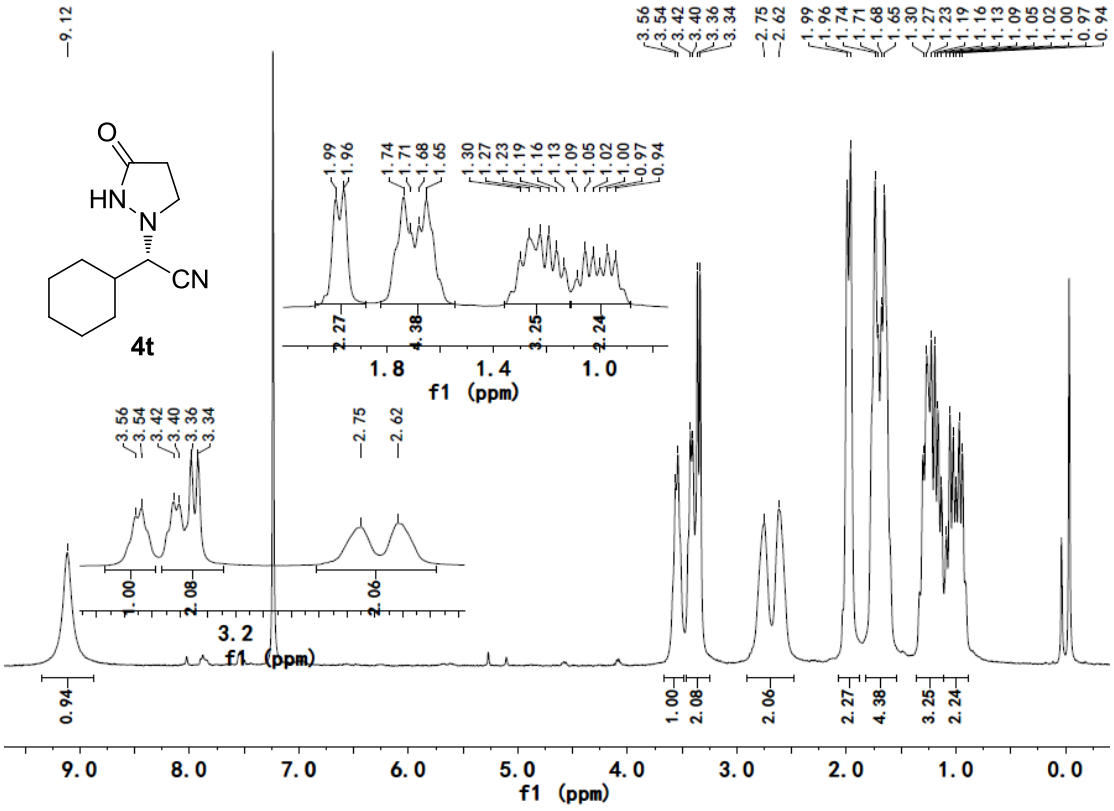


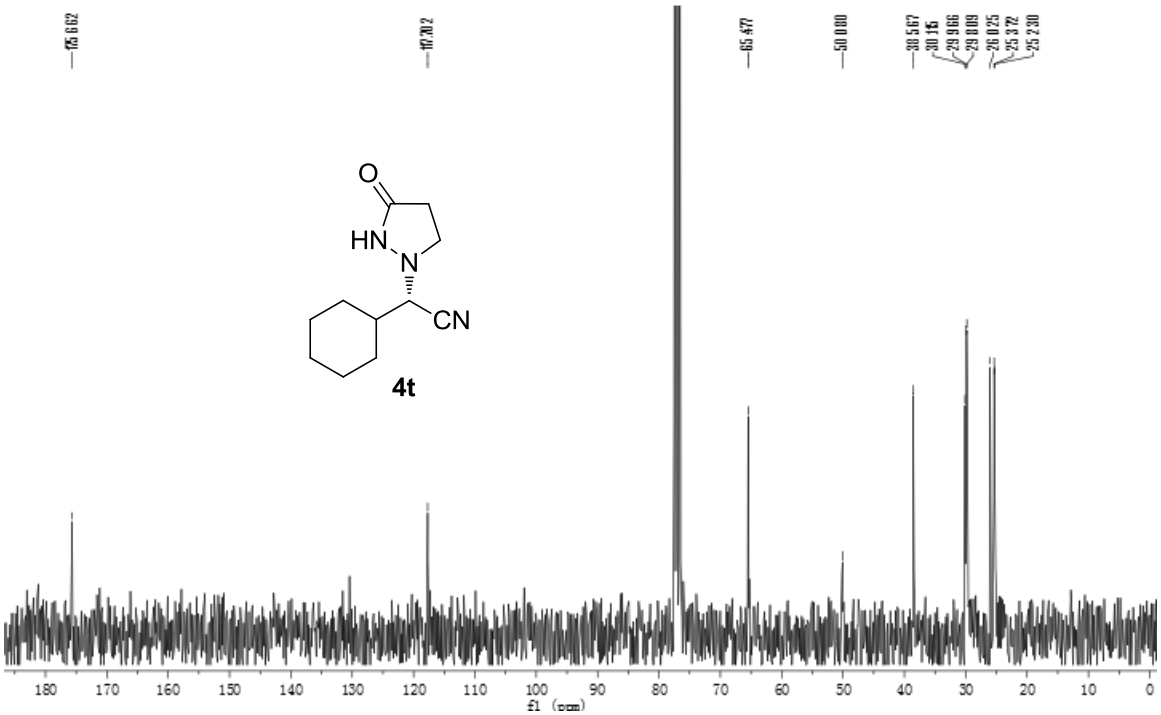
4-(cyano(3-oxopyrazolidin-1-yl)methyl) benzonitrile 4r



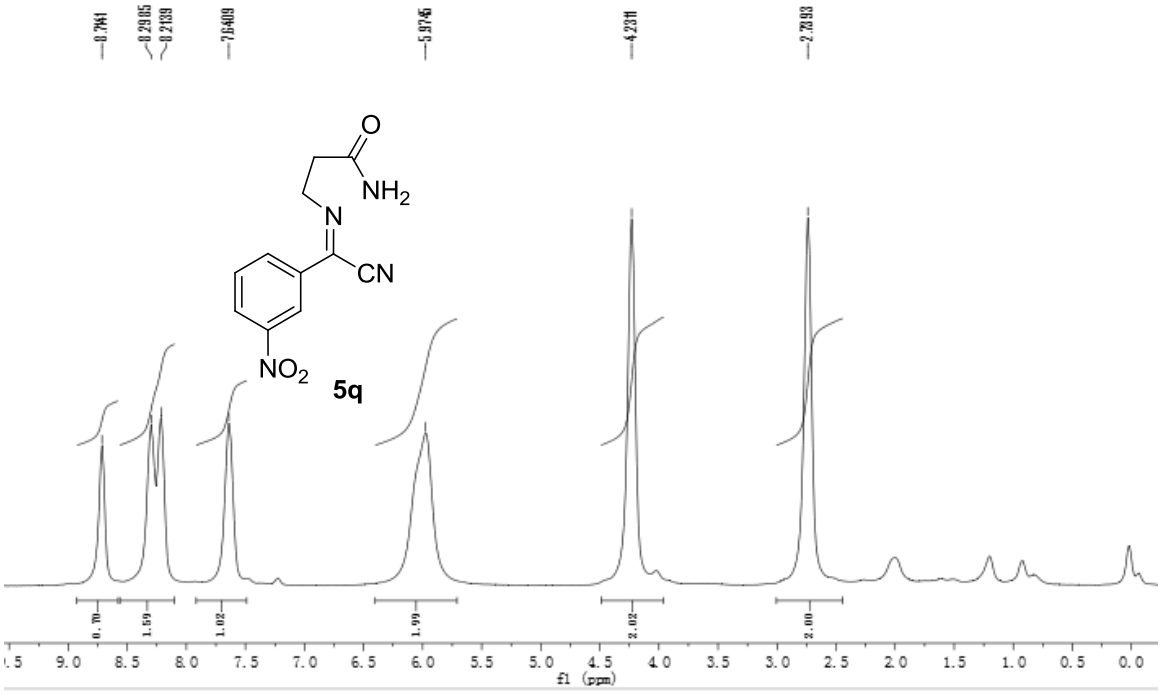


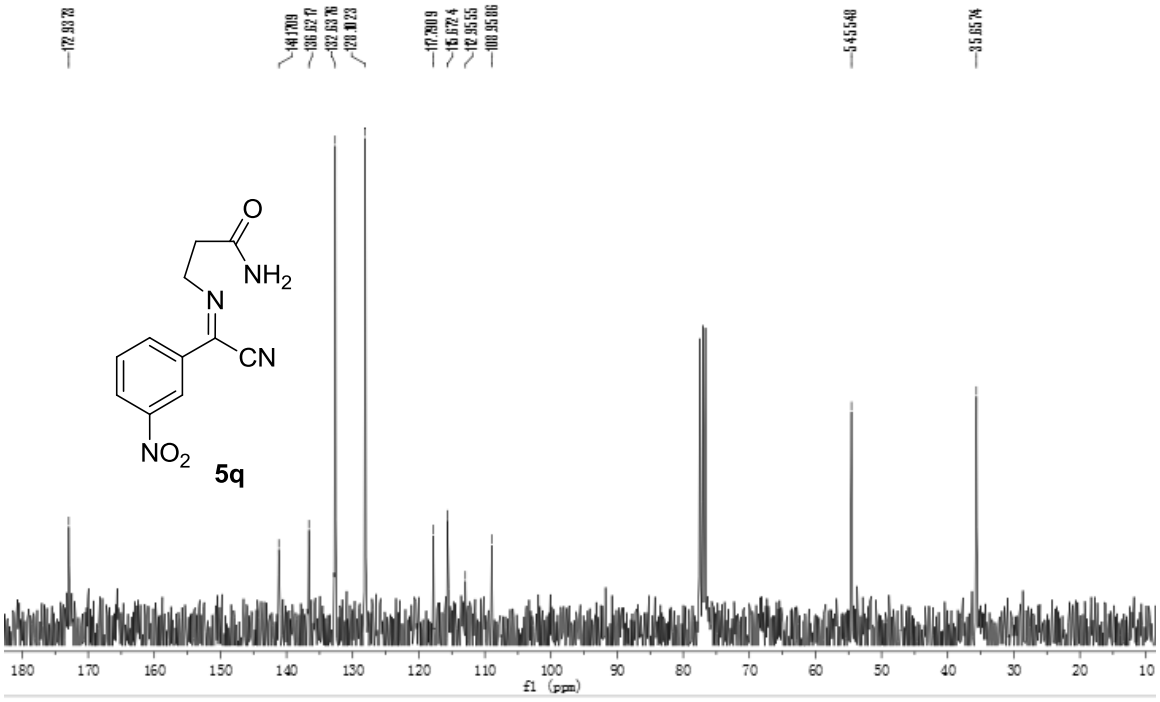
2-cyclohexyl-2-(3-oxopyrazolidin-1-yl) acetonitrile 4t



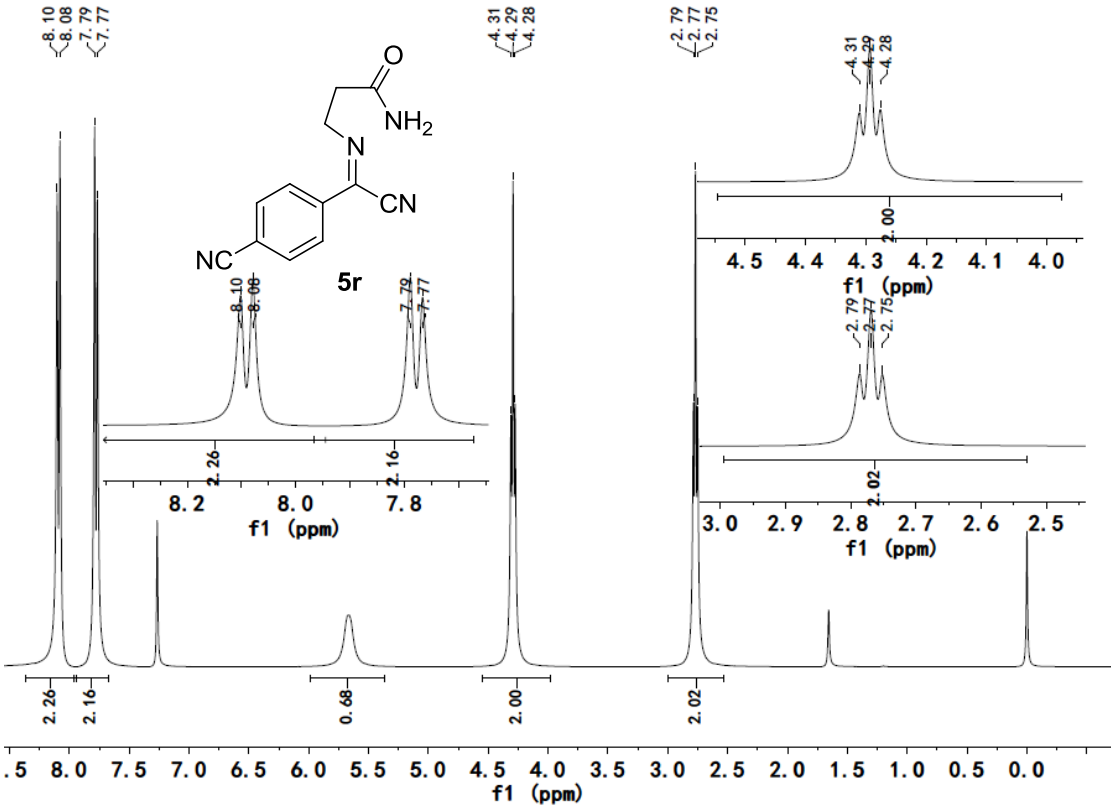


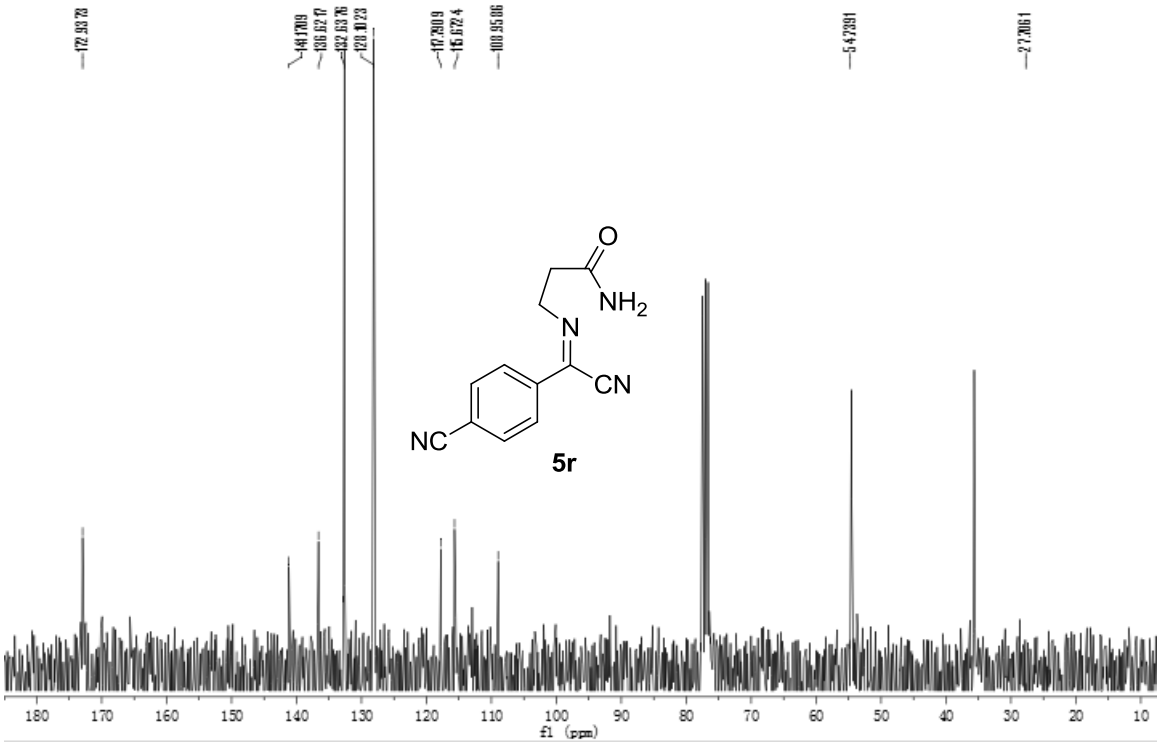
3-(cyano(3-nitrophenyl)methyleneamino)propanamide 5q



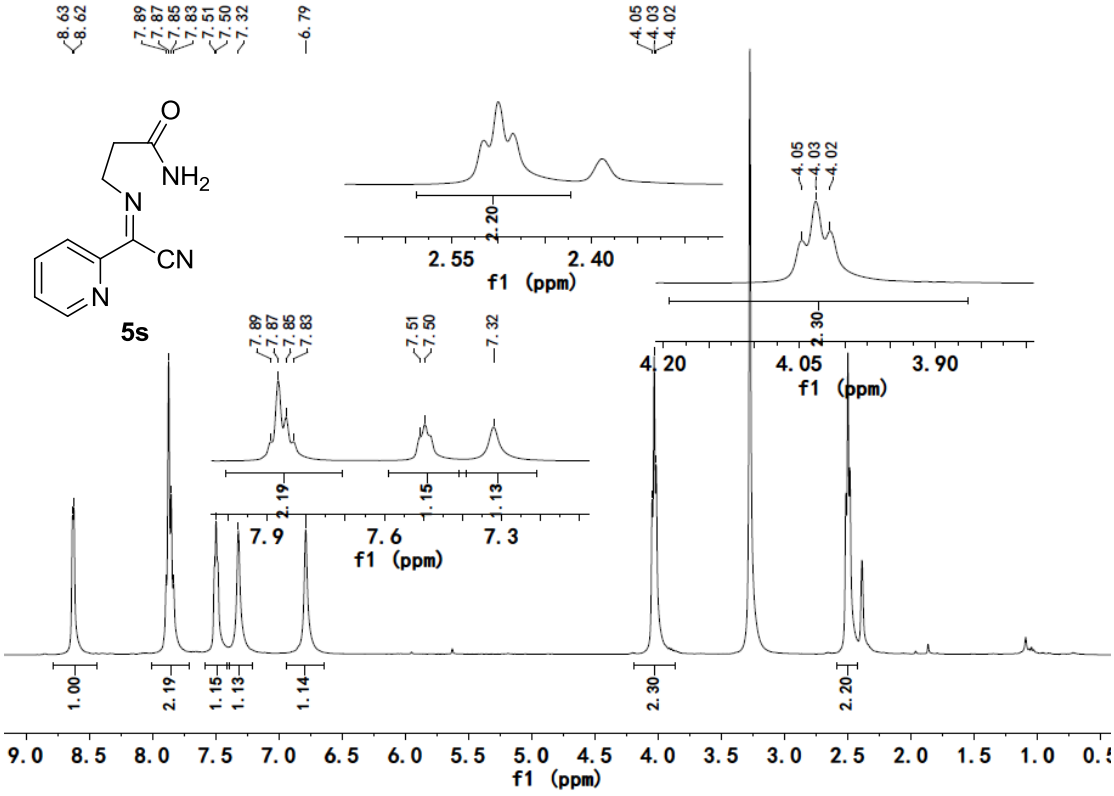


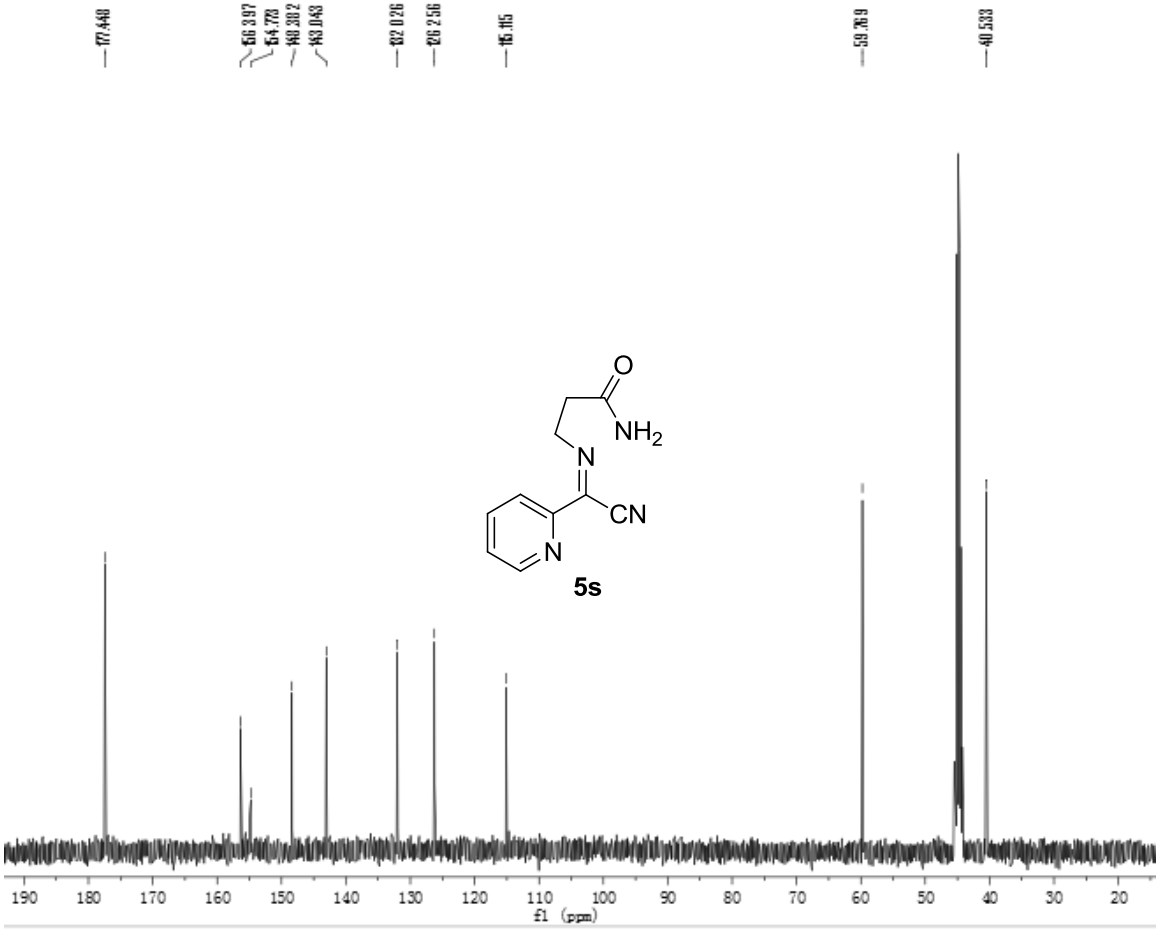
3-(cyano(4-cyanophenyl)methyleneamino)propanamide 5r





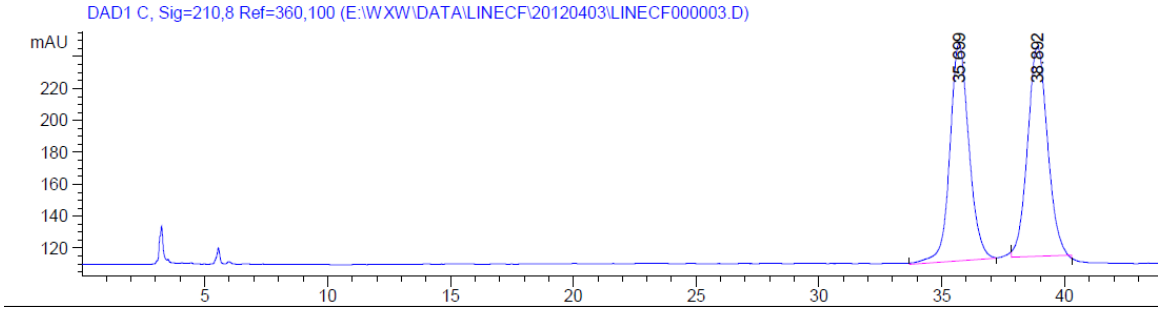
3-(cyano(pyridin-2-yl)methyleneamino)propanamide 5s



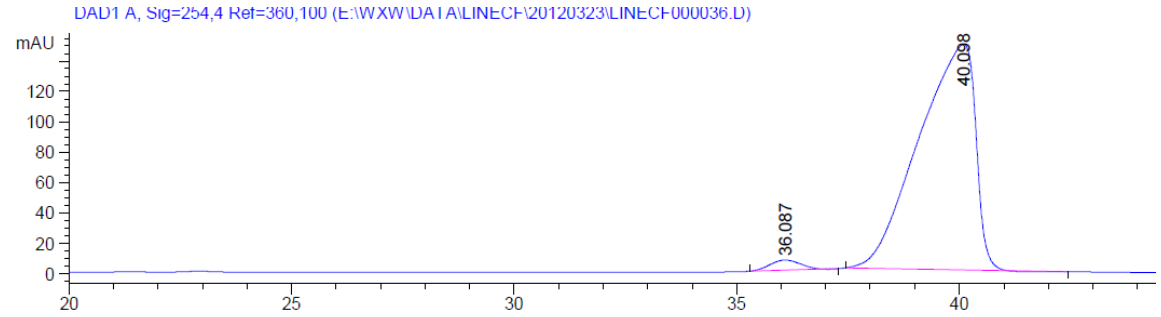


7. HPLC spectra

2-(3-oxopyrazolidin-1-yl)-2-phenylacetonitrile 4a

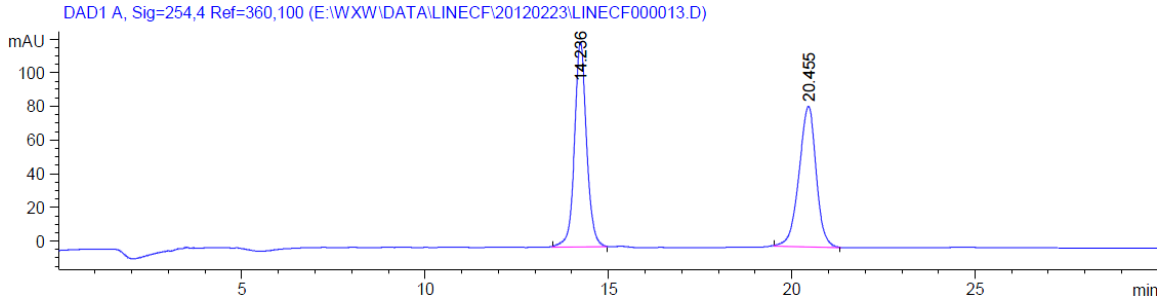


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.699	MM R	0.8984	7360.14795	136.54027	49.7985
2	38.892	MM R	0.9410	7419.69971	131.40828	50.2015

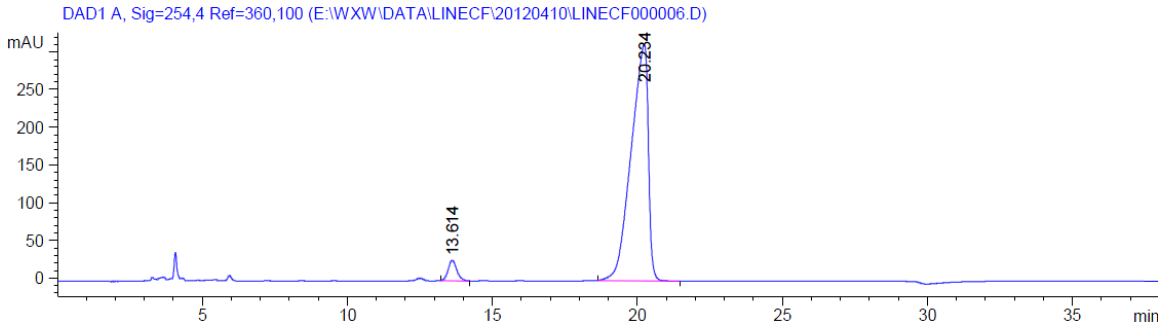


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.087	BB	0.6551	313.54459	6.71127	2.3352
2	40.098	BB	1.2240	1.31132e4	148.53275	97.6648

2-(2-fluorophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4b

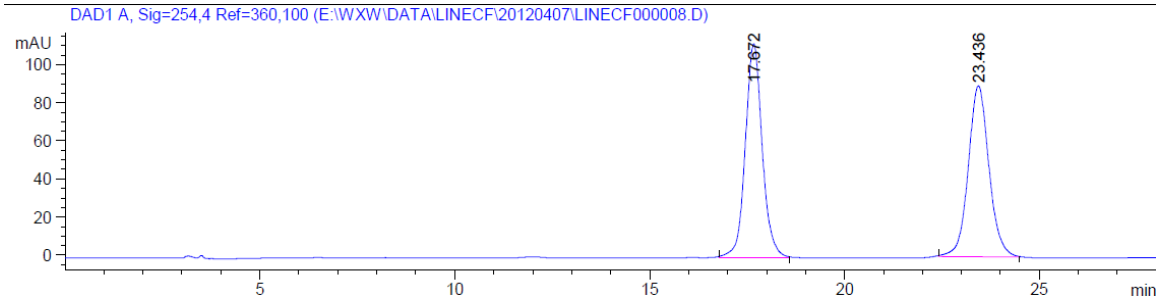


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.236	BB	0.3472	2787.46313	121.68956	50.6350
2	20.455	BB	0.4958	2717.54639	83.47952	49.3650

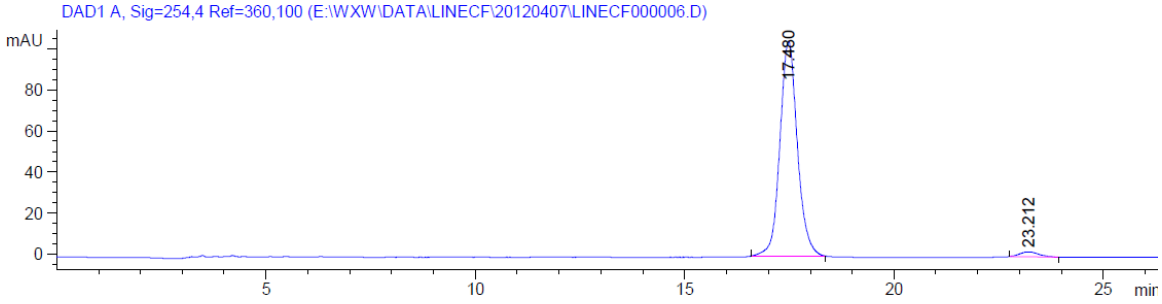


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.614	BB	0.3171	571.71259	27.43616	4.2454
2	20.234	BB	0.6627	1.28951e4	314.30371	95.7546

2-(4-fluorophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4c

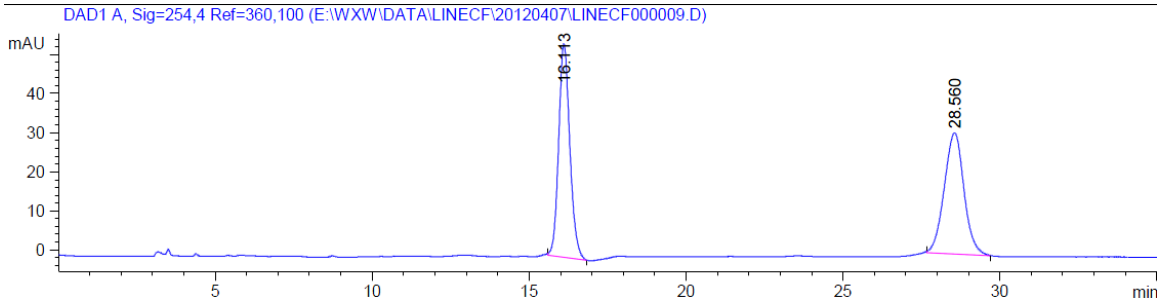


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.672	BB	0.4593	3379.40869	112.24490	50.3348
2	23.436	BB	0.5650	3334.45654	89.83614	49.6652

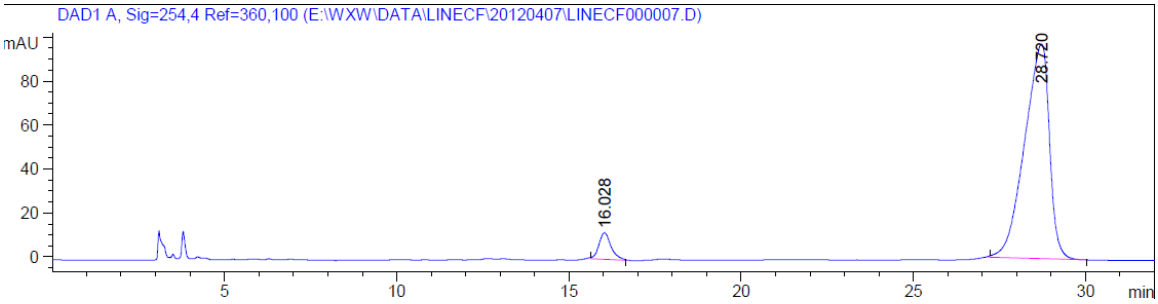


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.480	BB	0.4466	3064.14331	104.96231	97.4067
2	23.212	BB	0.4639	81.57852	2.53192	2.5933

2-(2-chlorophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4d

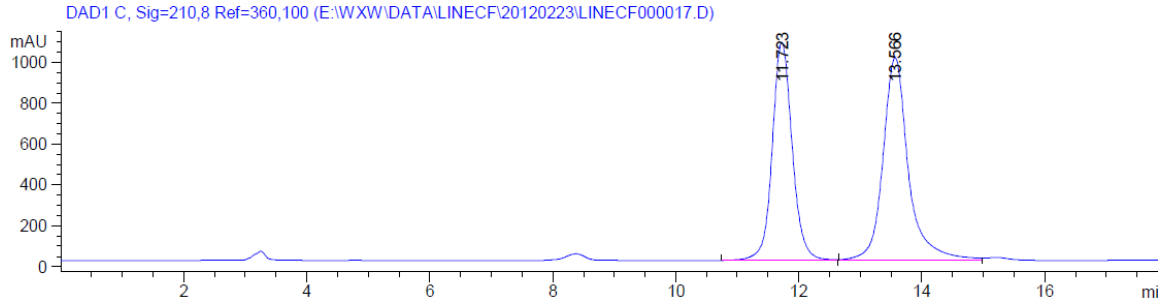


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.113	BB	0.3806	1349.76880	54.55830	49.8574
2	28.560	BB	0.6746	1357.49060	31.01432	50.1426

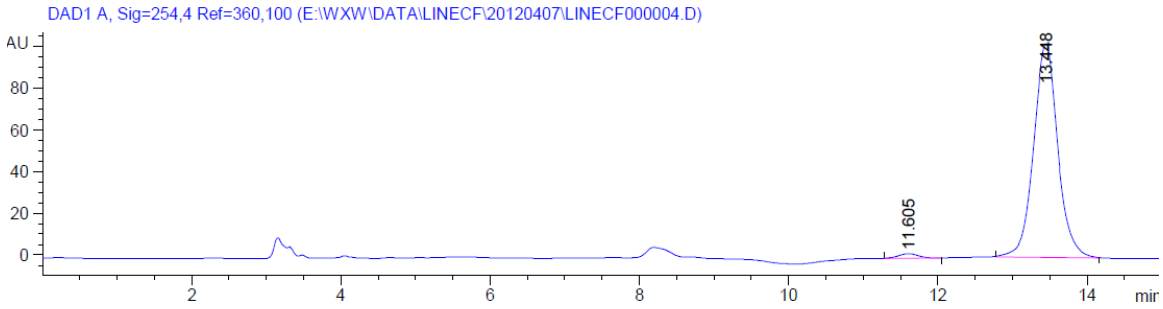


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.028	BB	0.3714	298.72064	12.12578	5.7387
2	28.720	BB	0.7656	4906.63574	97.74610	94.2613

2-(3-chlorophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4e

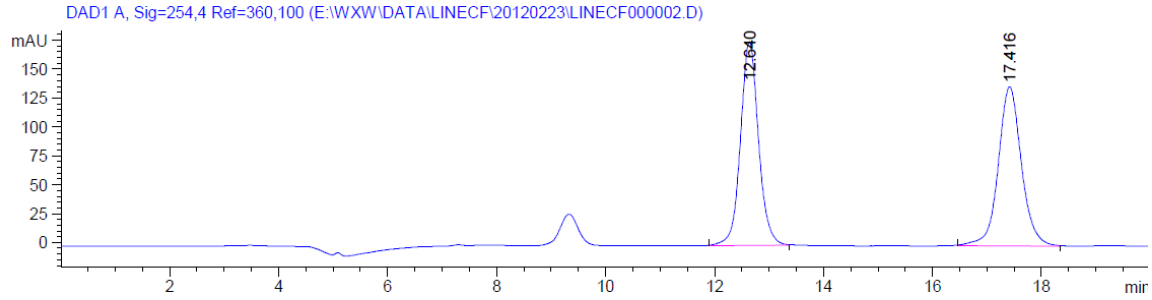


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.723	MM R	0.3691	2.35014e4	1061.22424	49.6437
2	13.566	MM R	0.4216	2.38387e4	942.37604	50.3563

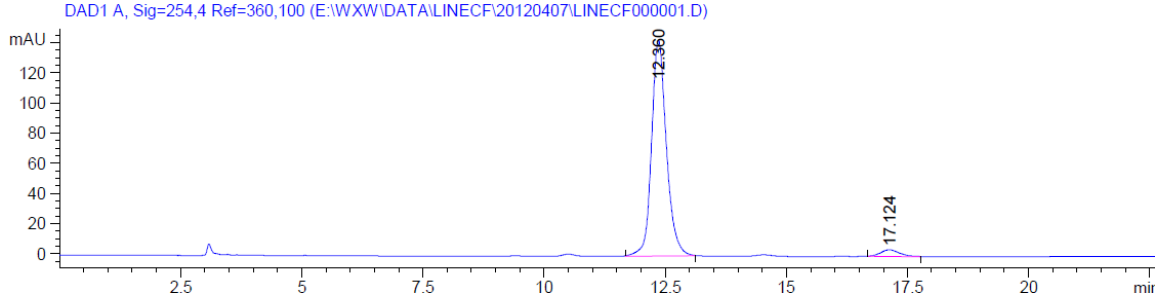


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.605	BB	0.2742	39.76666	2.16546	1.6989
2	13.448	BB	0.3419	2300.96021	102.48891	98.3011

2-(4-chlorophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4f

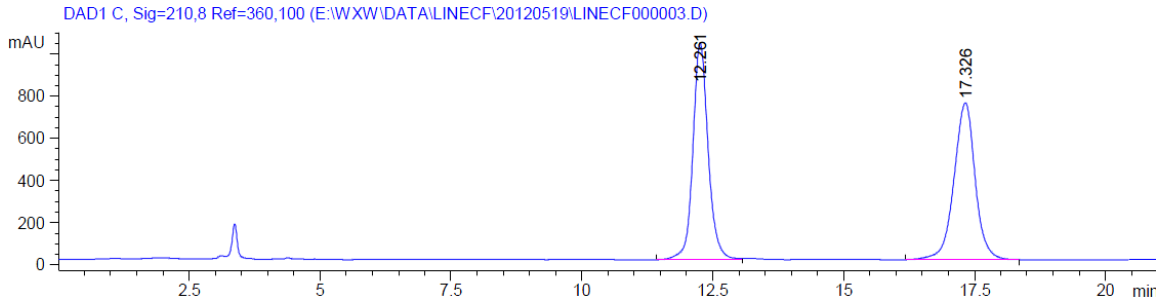


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.640	BB	0.3504	4049.04150	176.00130	49.9650
2	17.416	BB	0.4482	4054.71460	137.43324	50.0350

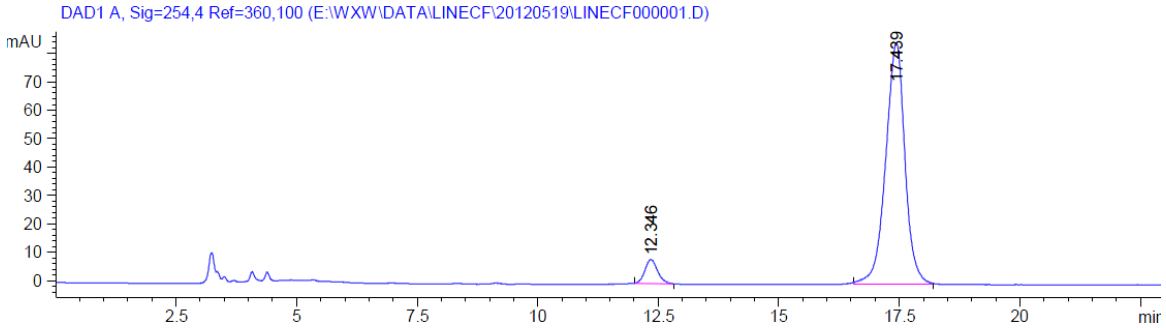


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.360	BB	0.3252	3060.18994	143.23972	96.2967
2	17.124	BB	0.4002	117.68716	4.45558	3.7033

2-(2-bromophenyl)-2-(3-oxopyrazolidin-1-yl)acetonitrile 4g

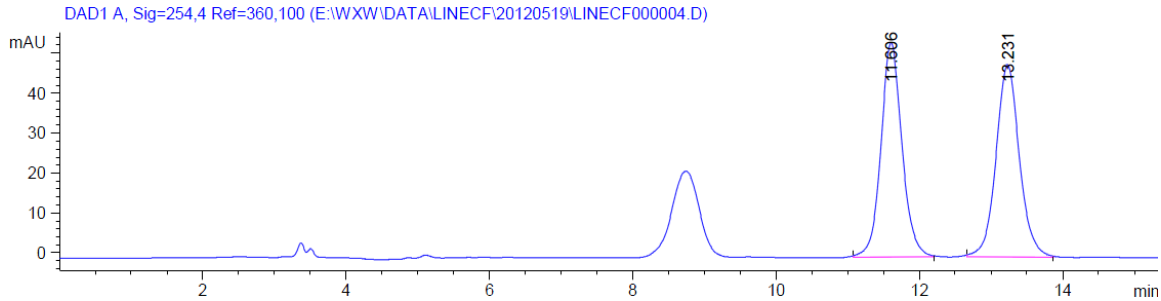


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.261	BB	0.3072	2.09142e4	1028.49902	49.8717
2	17.326	BB	0.4292	2.10218e4	745.10242	50.1283

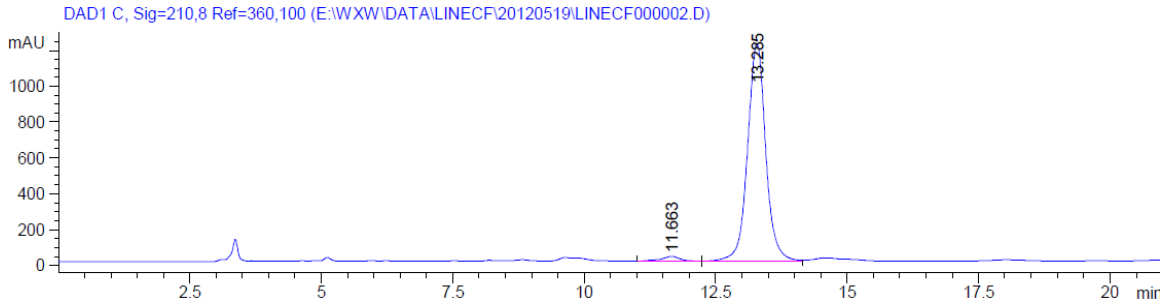


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.347	BB	0.2963	1860.92944	95.09286	6.7739
2	17.439	BB	0.4337	2.56109e4	900.92346	93.2261

2-(3-bromophenyl)-2-(3-oxopyrazolidin-1-yl)acetonitrile 4h

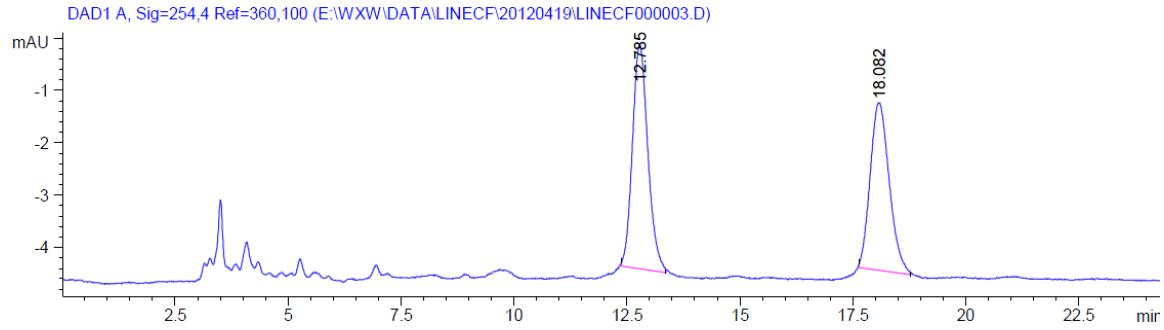


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.606	BB	0.3098	1092.95337	53.62835	50.0519
2	13.231	BB	0.3441	1090.68726	48.18037	49.9481

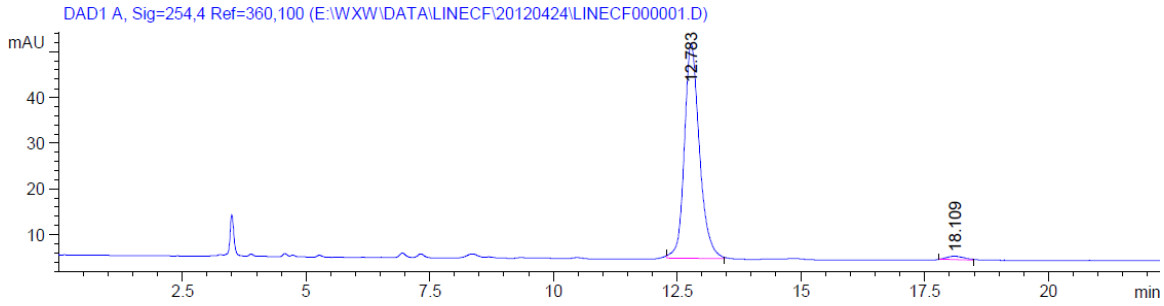


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.663	VV	0.3645	686.33545	27.00343	2.2903
2	13.285	VV	0.3671	2.92802e4	1215.23230	97.7097

2-(4-bromophenyl)-2-(3-oxopyrazolidin-1-yl)acetonitrile 4i

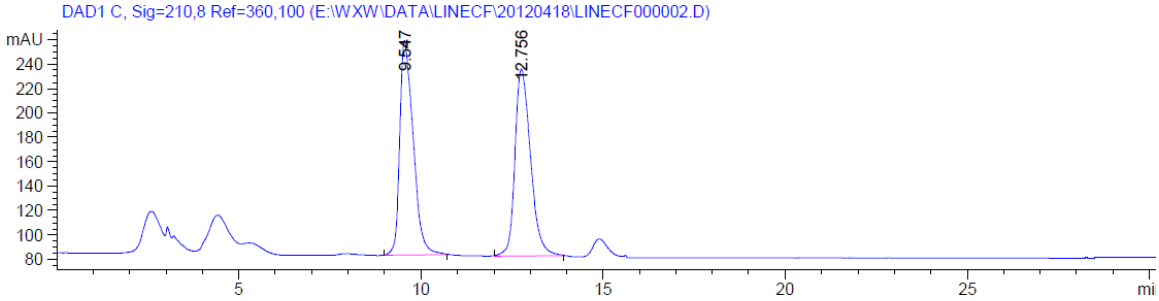


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.785	BB	0.3610	101.86327	4.29036	49.8044
2	18.082	MM	0.5150	102.66332	3.32259	50.1956

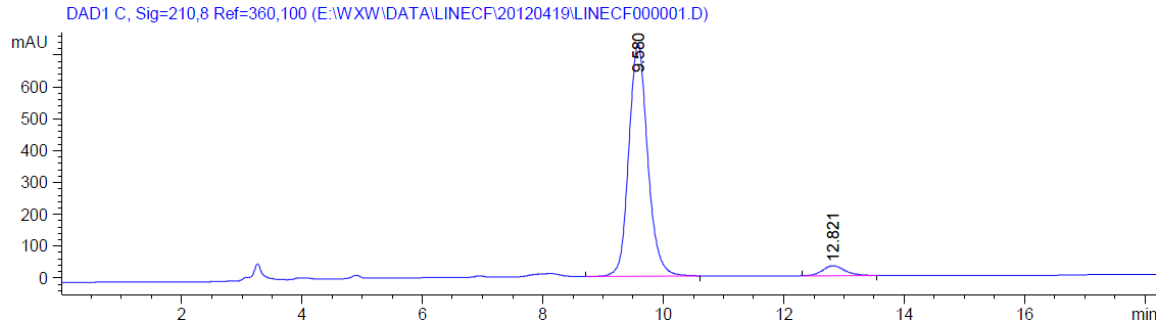


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.783	BB	0.3208	996.08496	47.08492	98.2886
2	18.109	MM R	0.3859	17.34409	7.49047e-1	1.7114

2-(3-oxopyrazolidin-1-yl)-2-(4-(trifluoromethyl)phenyl)acetonitrile 4j

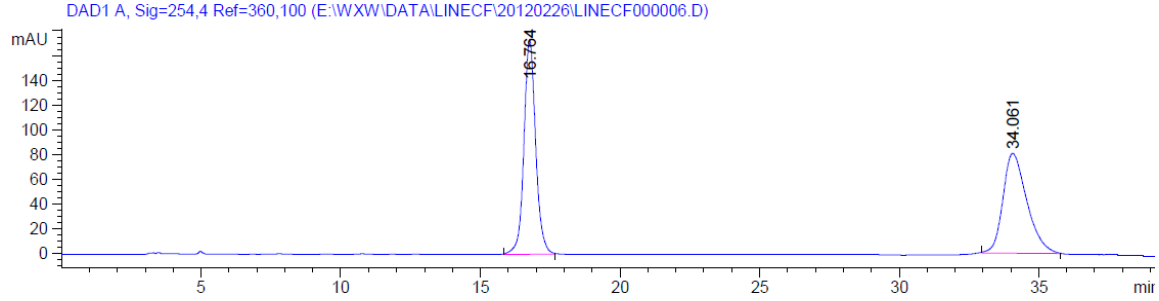


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.547	BB	0.3701	4520.15527	175.72083	49.7712
2	12.756	BB	0.4651	4561.71875	153.34102	50.2288

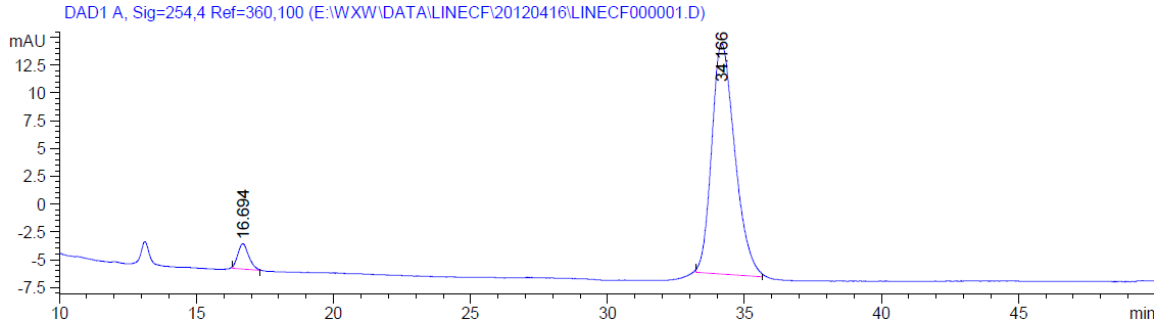


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.580	VB	0.3405	1.59127e4	729.43243	95.1122
2	12.821	BB	0.3984	817.74750	31.14148	4.8878

2-(2-methoxyphenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4k

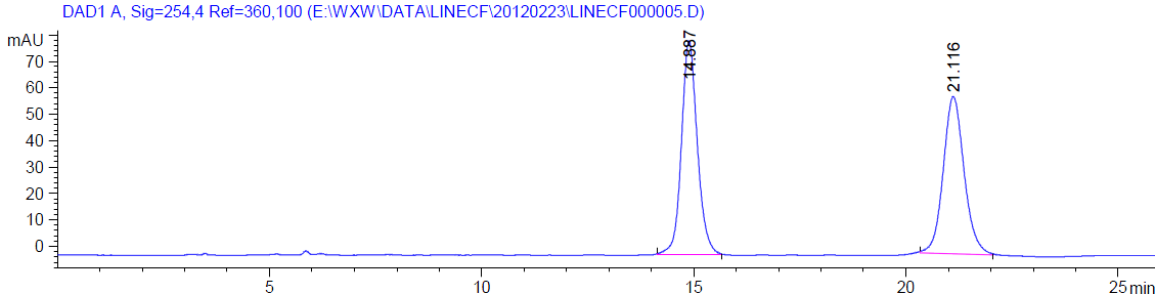


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.764	BB	0.4433	5534.51807	190.28606	50.9221
2	34.061	BB	0.8988	5334.06934	88.80187	49.0779

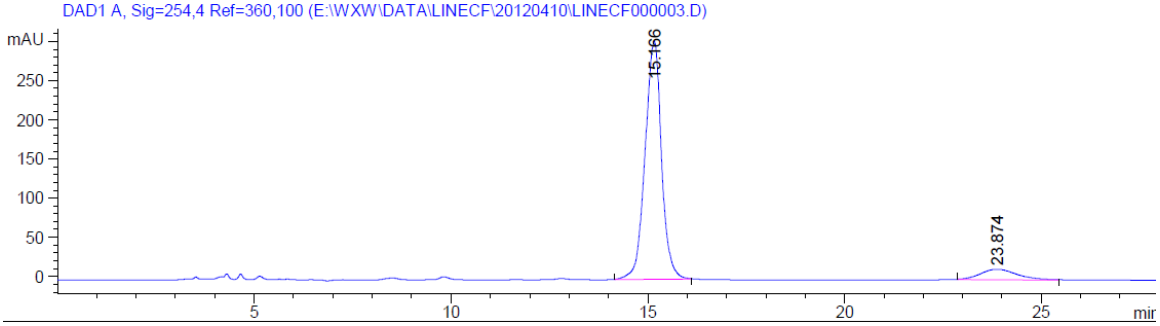


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.694	BB	0.4189	63.37877	2.27561	4.9423
2	34.166	BB	0.8693	1218.98633	20.75125	95.0577

2-(4-methoxyphenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4l

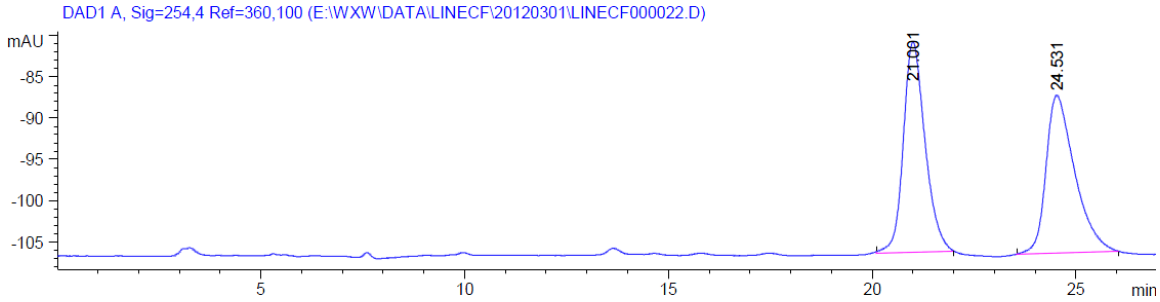


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.887	BB	0.3982	2109.40503	80.90417	50.8536
2	21.116	BB	0.5221	2038.59180	59.44609	49.1464

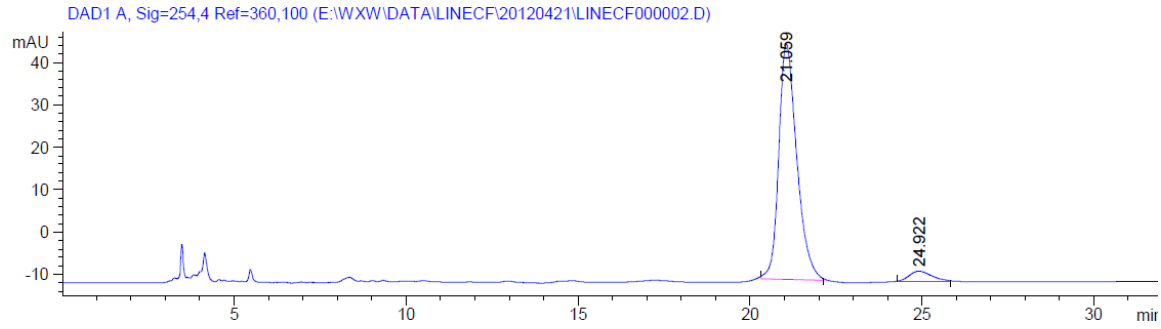


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.166	BB	0.4478	8863.46680	304.33228	91.3506
2	23.874	BB	0.9280	839.22040	13.16070	8.6494

2-(3, 5-dimethoxyphenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4m

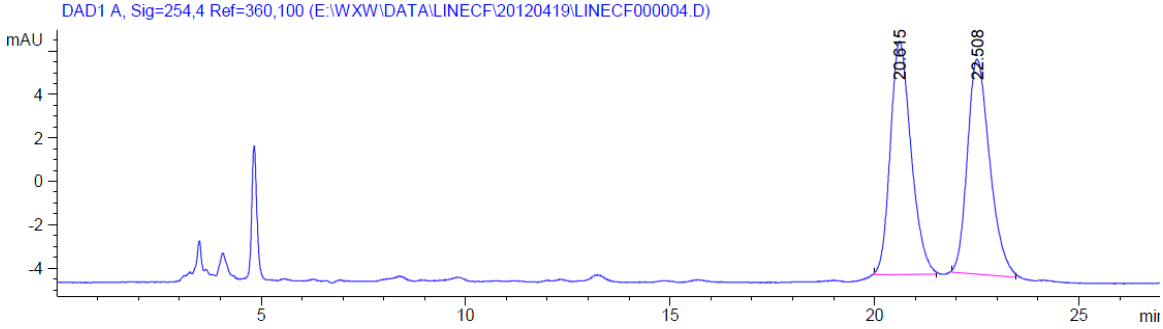


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.001	MM R	0.6179	942.54315	25.42359	50.3058
2	24.531	MM R	0.8146	931.08521	19.04945	49.6942

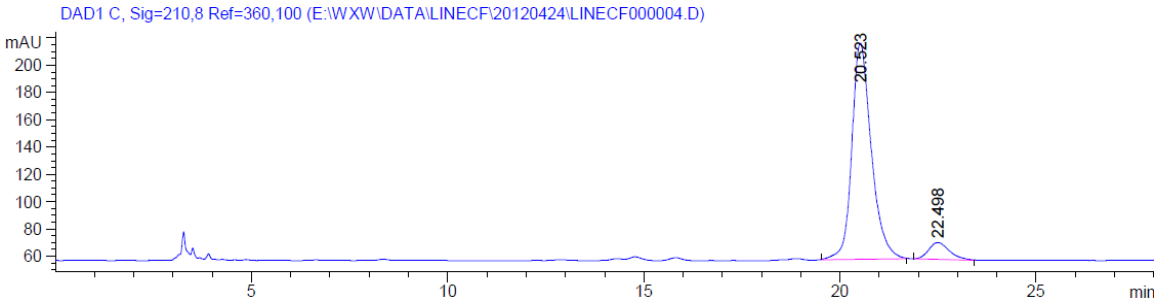


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.059	BB	0.5580	2026.24316	55.49463	95.0461
2	24.922	MM R	0.7464	105.60909	2.35826	4.9539

2-(benzo[d][1,3]dioxol-5-yl)-2-(3-oxopyrazolidin-1-yl)acetonitrile 4n

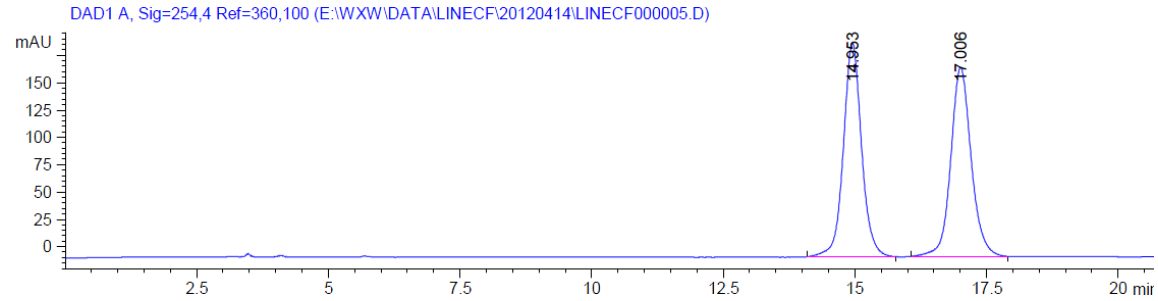


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.615	BB	0.5364	379.36777	10.73183	50.1737
2	22.508	BB	0.5634	376.74094	9.91358	49.8263

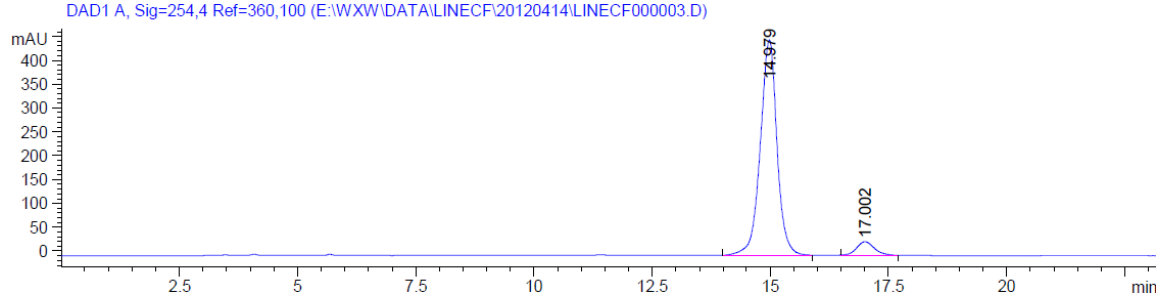


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.523	BB	0.5220	5476.98877	158.15971	92.5311
2	22.498	BB	0.5370	442.08966	12.25114	7.4689

2-(naphthalen-2-yl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4o

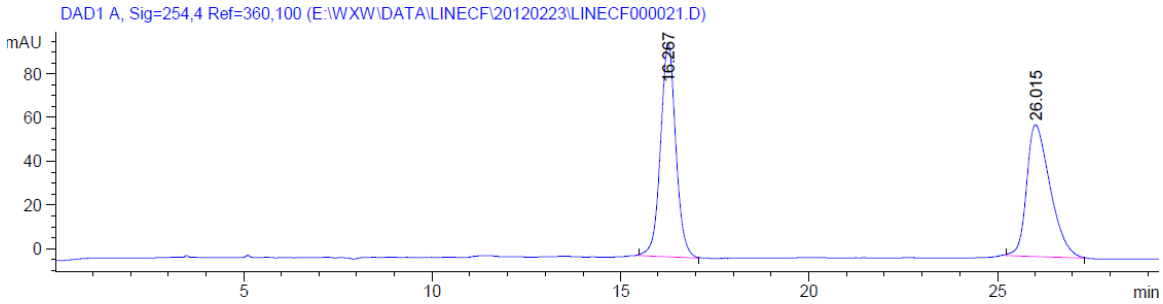


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.953	BB	0.3646	4713.05713	195.93488	50.1266
2	17.006	BB	0.4102	4689.25000	173.04314	49.8734

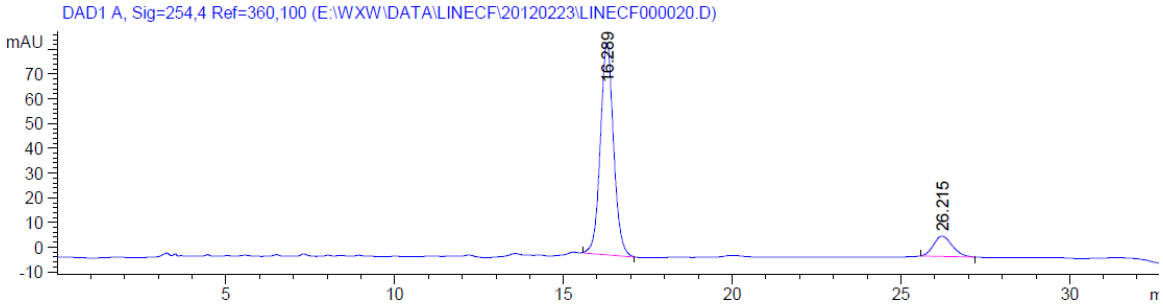


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.979	BB	0.3736	1.11436e4	452.04181	93.6806
2	17.002	BB	0.4015	751.71332	28.52491	6.3194

2-(furan-2-yl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4p

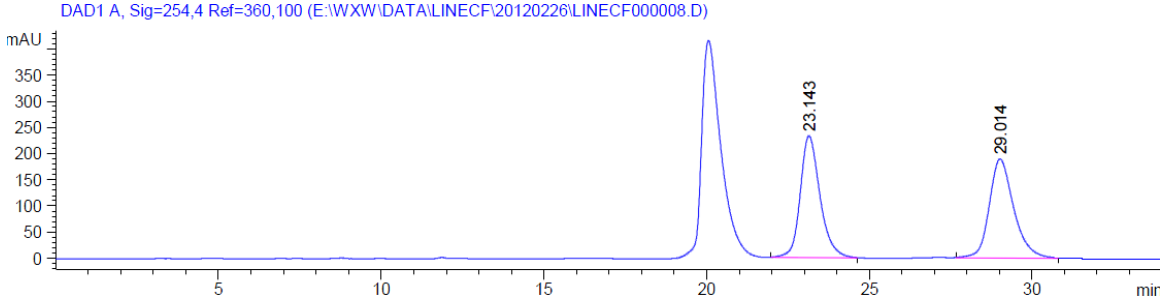


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.267	BB	0.4300	3081.76465	109.59901	51.1684
2	26.016	BB	0.6590	2941.02759	67.68298	48.8316

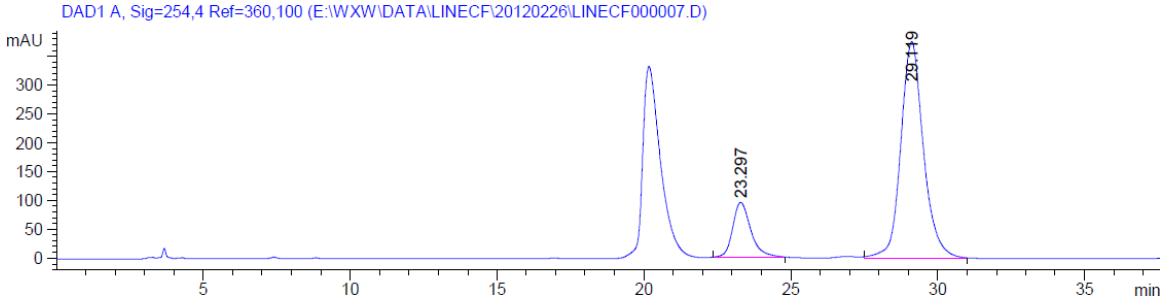


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.289	BB	0.4168	2330.33423	85.82217	87.9664
2	26.215	BB	0.5917	318.78488	8.19775	12.0336

2-(3-nitrophenyl)-2-(3-oxopyrazolidin-1-yl) acetonitrile 4q

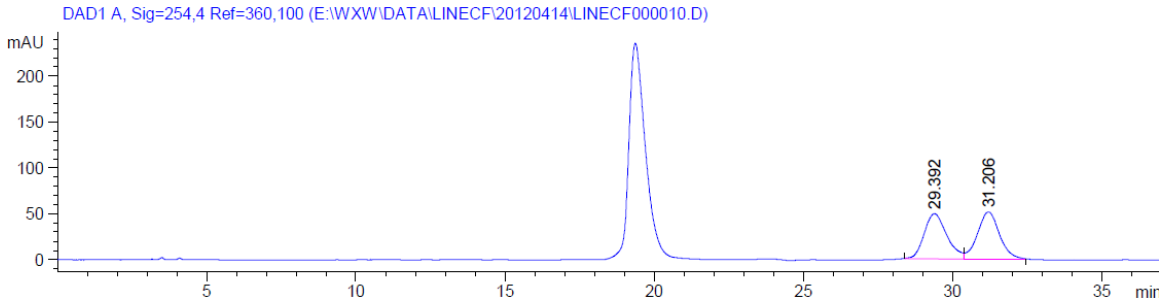


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.143	BB	0.6415	9830.99121	232.40099	49.9584
2	29.014	BB	0.7855	9847.37207	189.09953	50.0416

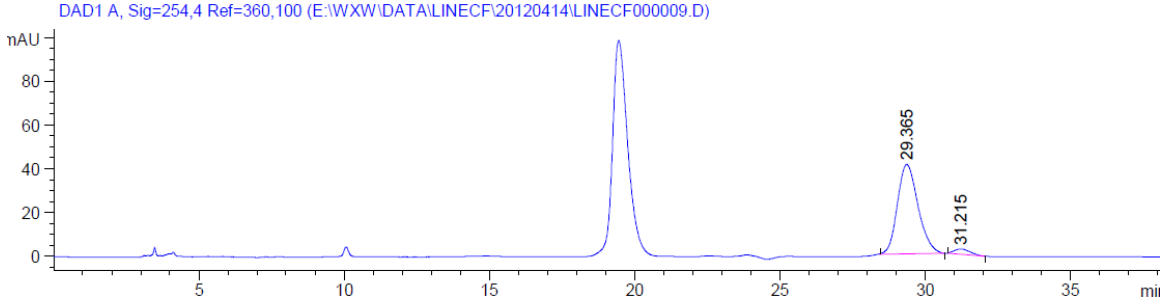


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.297	BB	0.6508	4119.61230	95.58554	17.0196
2	29.119	BB	0.8122	2.00855e4	375.38516	82.9804

4-(cyano(3-oxopyrazolidin-1-yl)methyl)benzonitrile 4r

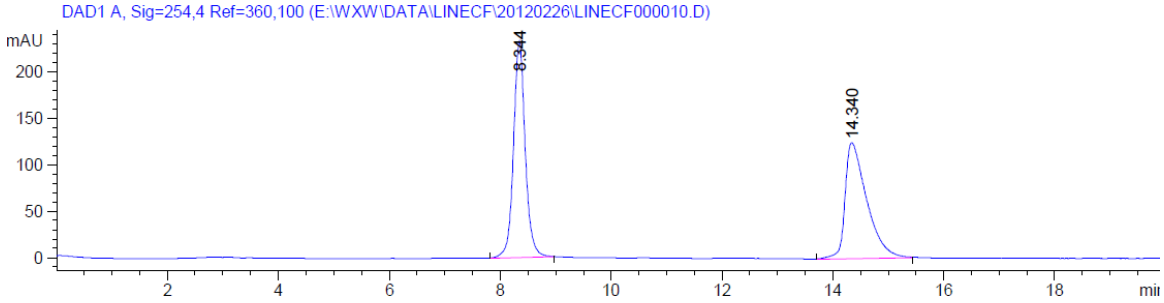


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.392	BV	0.8048	2599.50513	49.16806	49.4882
2	31.206	VB	0.7873	2653.26904	51.48138	50.5118

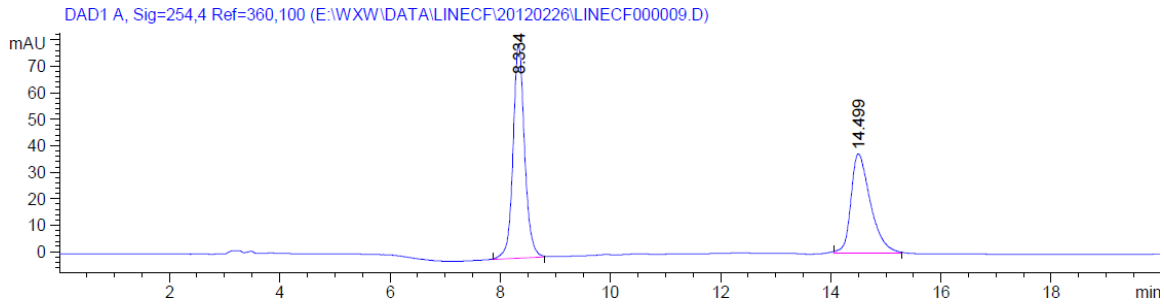


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.365	BB	0.7458	2014.34387	40.81464	95.8044
2	31.215	BB	0.4780	88.21461	2.32841	4.1956

2-cyclohexyl-2-(3-oxopyrazolidin-1-yl) acetonitrile 4t



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.344	BB	0.2238	3430.00903	232.91977	50.3768
2	14.340	BB	0.4047	3378.70410	124.47782	49.6232



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.334	BB	0.2189	1172.36548	80.96501	56.0850
2	14.499	BB	0.3718	917.97308	37.47684	43.9150