

Highly Enantioselective Phosphination and Hydrophosphonylation of Azomethine Imines: Using Chiral Squaramide as Hydrogen Bonding Organocatalyst

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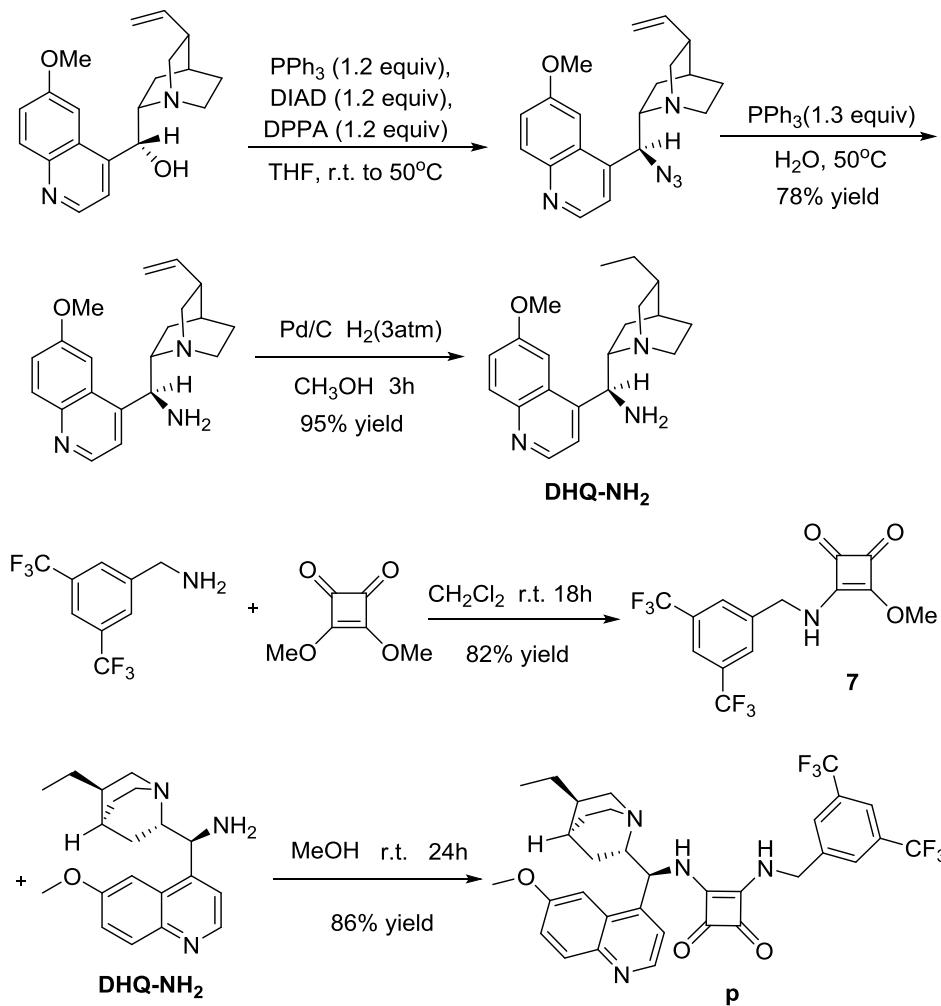
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1. General procedure for the preparation of catalysts

Catalyst **1a-1k**¹ and **1l-1p**² which were described in this paper were prepared according to the similar reported procedures. 9-amino (9-deoxy) epi-quinine was obtained via the classic Mitsunobu and Staudinger reactions from quinine; subsequently transformed into isothiocyanate which was used as a common electrophile in the following reactions with corresponding primary amines to give those catalysts.

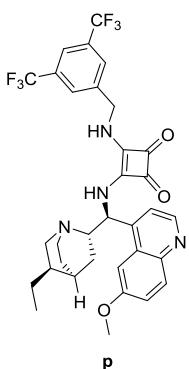
Procedure for the preparation of squaramide **p** derived from dihydroquinine



To a solution of **7** (2.12 g, 6 mmol) in MeOH (60 mL) was added a solution of DHQ-NH₂³ (1.63 g, 5 mmol) in MeOH (16 mL). After 24 h, the reaction mixture was filtered, and the precipitate was washed with cold MeOH (3 × 20 mL) to afford squaramide **p** (2.78g, 86 %) as a pale yellow solid.⁴

3-((3,5-bis(trifluoromethyl)benzyl)amino)-4-(((1S)-((2S,4S,5R)-5-ethylquinuclidin-2-yl)(6-methoxyquinolin-4-yl)methyl)amino)cyclobut-3-ene-1,2-dione Catalyst (**p**)

Pale yellow solid, mp 150-152 °C; $[\alpha]_D^{20} = -18.25(c\ 0.4, \text{CHCl}_3)$; ¹H NMR (400 MHz, CDCl₃) δ 8.58 (d, *J* = 4.3 Hz, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.68 (d, *J* = 20.2 Hz, 4H), 7.44 (d, *J* = 4.5 Hz,



p 1H), 7.36 (dd, $J = 9.2, 2.4$ Hz, 1H), 6.14 (s, 1H), 4.67 (s, 2H), 3.87 (s, 3H), 3.57 – 3.27 (m, 2H), 3.13 (d, $J = 10.3$ Hz, 1H), 2.66 (s, 1H), 2.41 (d, $J = 11.5$ Hz, 1H), 1.65 (s, 2H), 1.55 – 1.34 (m, 3H), 1.32 – 1.08 (m, 3H), 0.75 (t, $J = 7.2$ Hz, 5H); ^{13}C NMR (101 MHz, CDCl_3) δ 182.99, 182.62, 167.76, 167.31, 158.69, 147.62, 144.76, 140.53, 132.53, 132.19, 131.86, 131.53, 127.97, 127.21, 124.50, 122.11, 121.79, 119.08, 57.54, 55.88, 46.94, 40.93, 36.74, 27.90, 27.33, 25.49, 24.89, 11.93; IR: 3208.2, 2960.9, 2931.5, 2866.7, 1795.3, 1668.7, 1621.6, 1586.3, 1533.3, 1509.7, 1460.3, 1432.4, 1376.7, 1343.6, 1277.2, 1238.9, 1165.3, 1124.1, 1028.5, 972.8, 892.7, 838.7, 729.3, 703.7, 682.6 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{33}\text{H}_{32}\text{F}_6\text{N}_4\text{O}_3[\text{M}+\text{H}]^+$: 647.2451; found: 647.2443, 1.3 ppm.

3. Reference

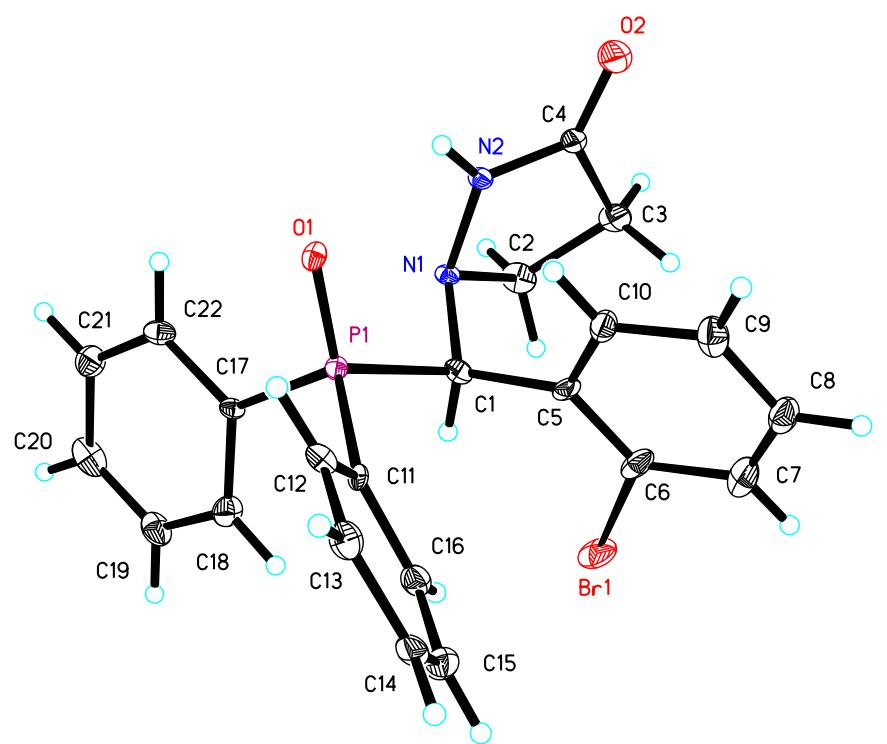
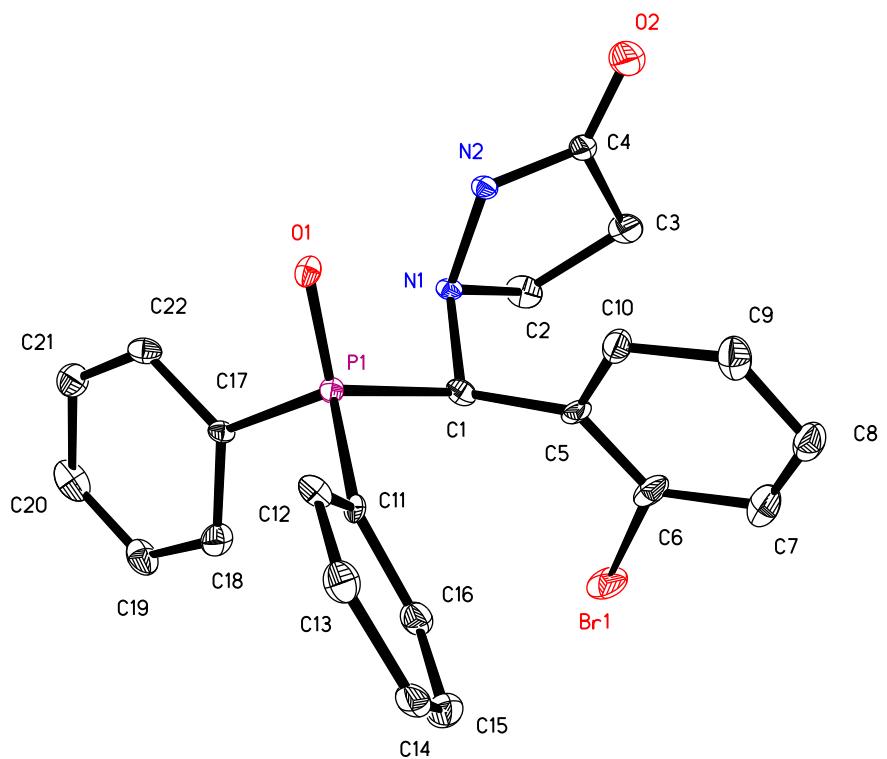
1. (a) M. Kaik, J. Gawroński, *Tetrahedron: Asymmetry* **2003**, *14*, 1559–1563; (b) B. Vakulya, S. Varga, A. Csámpai, T. Soós, *Org. Lett.* **2005**, *7*, 1967–1969; (c) C. K. Tan, L. Zhou, Y.-Y Yeung, *Org. Lett.* **2011**, *13*, 2738–2741. (d) Z.-W. Ma, Y.-X. Liu, P.-L. LiH., Ren, Y. Zhu, J.-C. Tao, *Tetrahedron: Asymmetry* **2011**, *22*, 1740–1748; (e) X. Shi, W. He, H. Li, X. Zhang, S. Y. Zhang, *Tetrahedron Lett.*, **2011**, *52*, 3204–3207; (f) N.-K. Li, Z.-M. Liu, X.-F. Huang, J.-X. Zhang, X. Chen, Y. Wang, X.-W. Wang, *RSC Adv.* **2013**, *3*, 9154–9157.
2. H. Y. Bae, S. Some, J. H. Lee, J.-Y. Kim, M. J. Song, S. Lee, Y. J. Zhang, C. E. Song, *Adv. Synth. Catal.* **2011**, *353* (17), 3196–3202.
3. (a) B. Vakulya, S. Varga, A. Csámpai, T. Soós, *Org. Lett.* **2005**, *7*, 1967–1969; (b) Palacio, C.; Connon, S. J., *Org. Lett.* **2011**, *13*, 1298–1301.
4. J. P. Malerich, K. Hagihara, V. H. Rawal, *J. Am. Chem. Soc.* **2008**, *130*, 14416–14417.

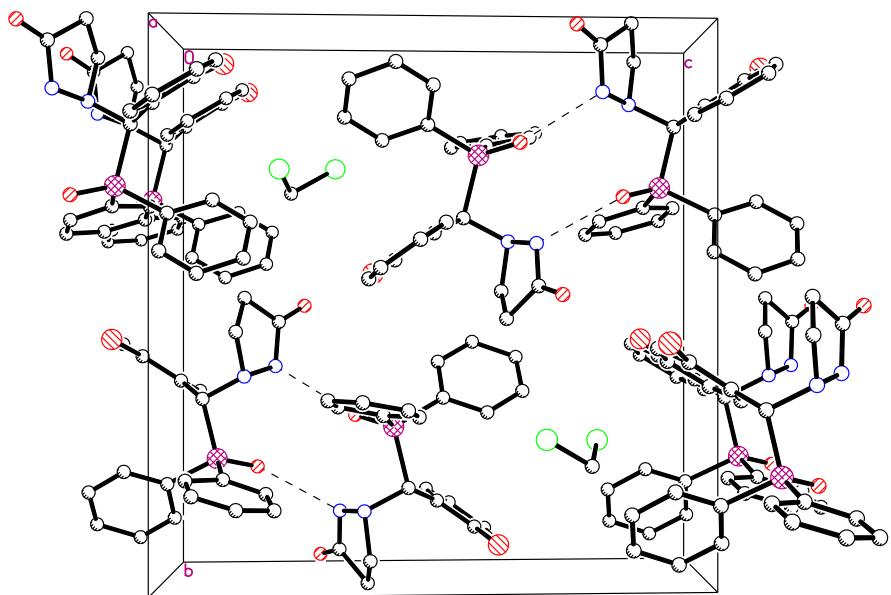
4. Single-Crystal X-ray Crystallography of 3g

Crystal data and structure refinement for **3g**

Identification code	mo_dm13290_0m
Empirical formula	C22.50 H21 Br Cl N2 O2 P
Formula weight	497.74
Temperature	140(2) K
	S3

Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 8.671(3) Å alpha = 90 deg. b = 15.948(6) Å beta = 94.150(7) deg. c = 15.692(6) Å gamma = 90 deg.
Volume	2164.3(14) Å ³
Z, Calculated density	4, 1.528 Mg/m ³
Absorption coefficient	2.119 mm ⁻¹
F(000)	1012
Crystal size	0.25 x 0.20 x 0.15 mm
Theta range for data collection	1.30 to 27.84 deg.
Limiting indices	-11<=h<=11, 0<=k<=20, 0<=l<=20
Reflections collected / unique	5219 / 5219 [R(int) = 0.0000]
Completeness to theta = 27.84	97.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7417 and 0.6194
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5219 / 1 / 533
Goodness-of-fit on F ²	1.074
Final R indices [I>2sigma (I)]	R1 = 0.0655, wR2 = 0.1762
R indices (all data)	R1 = 0.0812, wR2 = 0.1936
Absolute structure parameter	0.084(16)
Largest diff. peak and hole	1.910 and -1.126 e.Å ⁻³

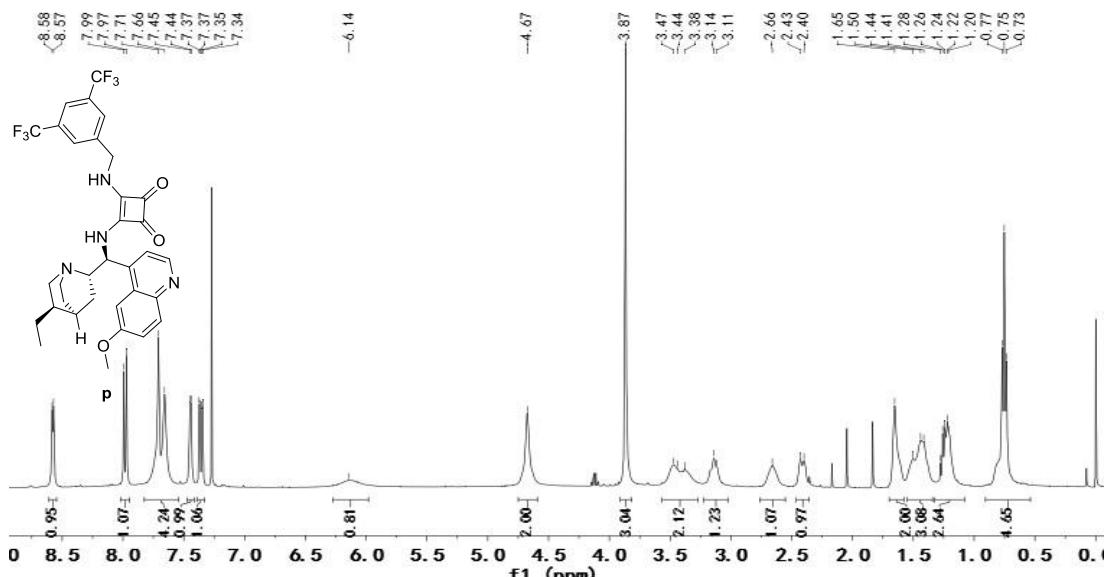


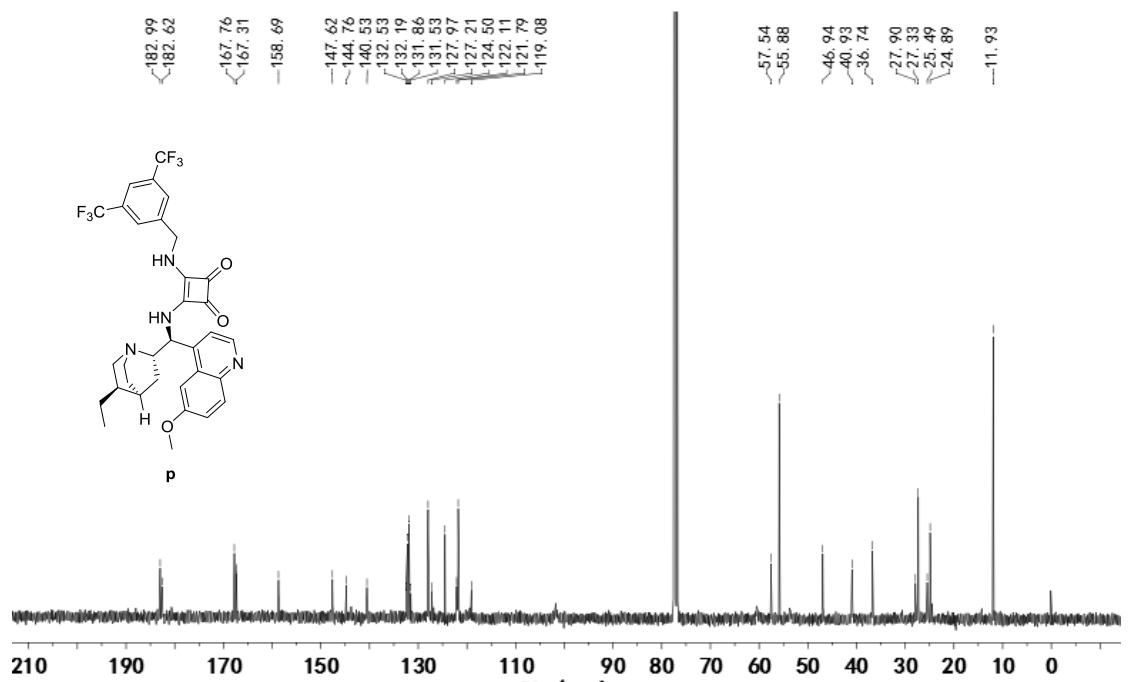


The crystal was prepared from the solution of **3g** in DCM and n-hexane. CCDC 941868 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

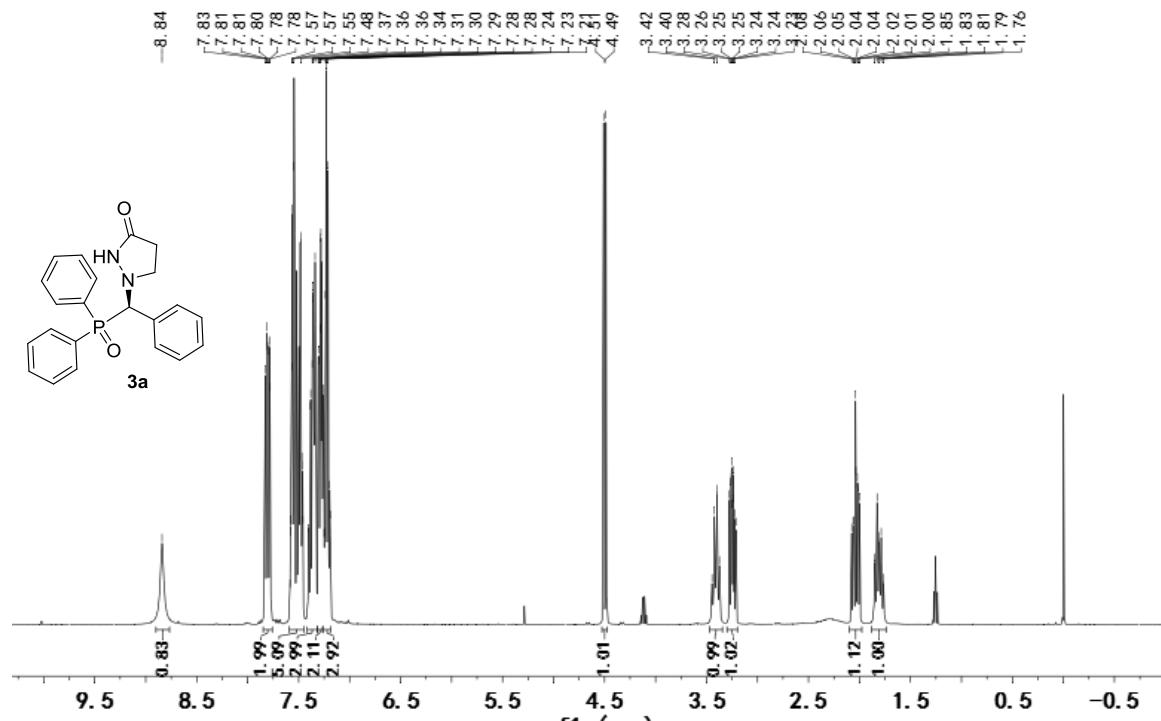
4. ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra

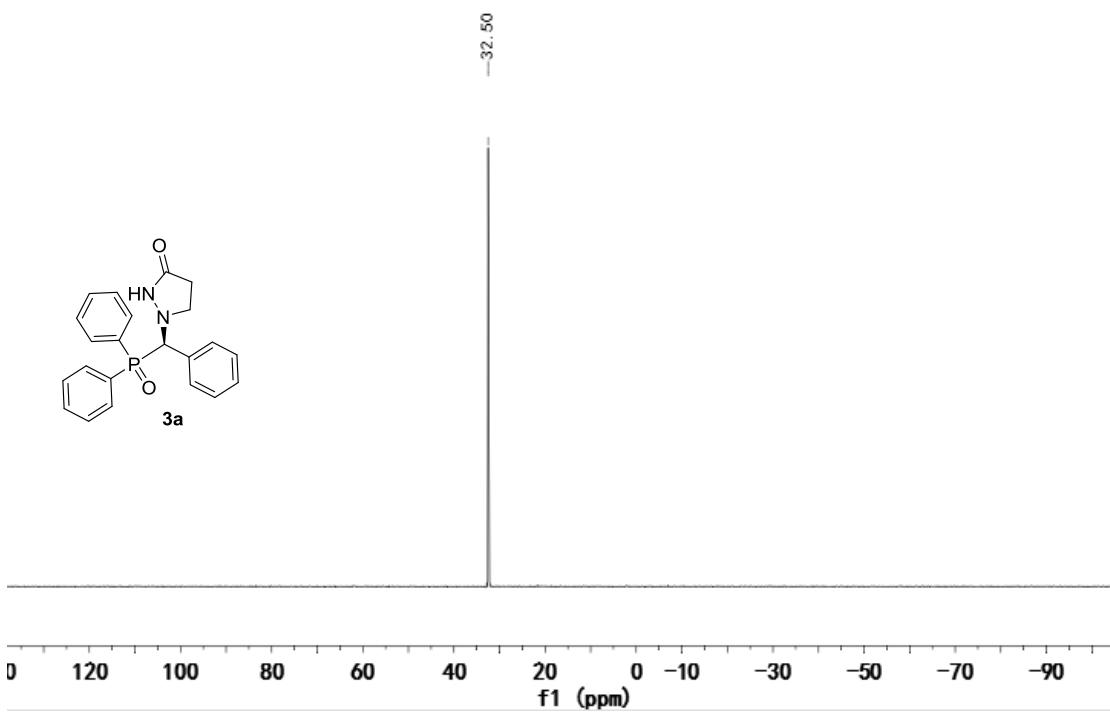
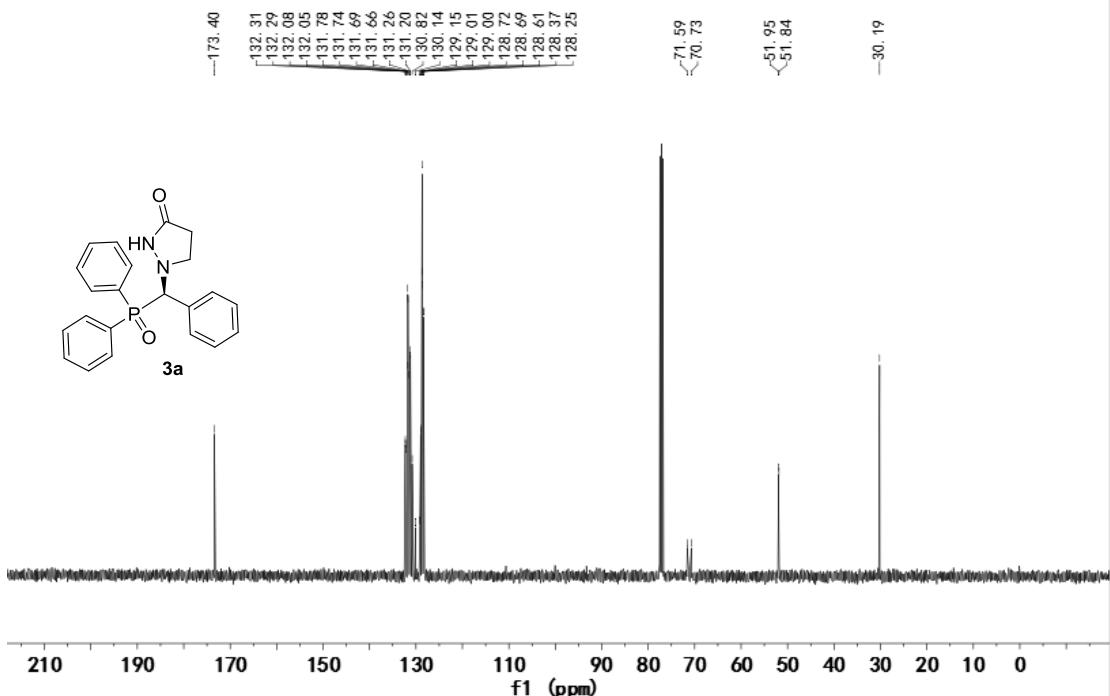
3-((3,5-bis(trifluoromethyl)benzyl)amino)-4-(((1S)-((2S,4S,5R)-5-ethylquinuclidin-2-yl)(6-methoxyquinolin-4-yl)methyl)amino)cyclobut-3-ene-1,2-dione Catalyst (p)



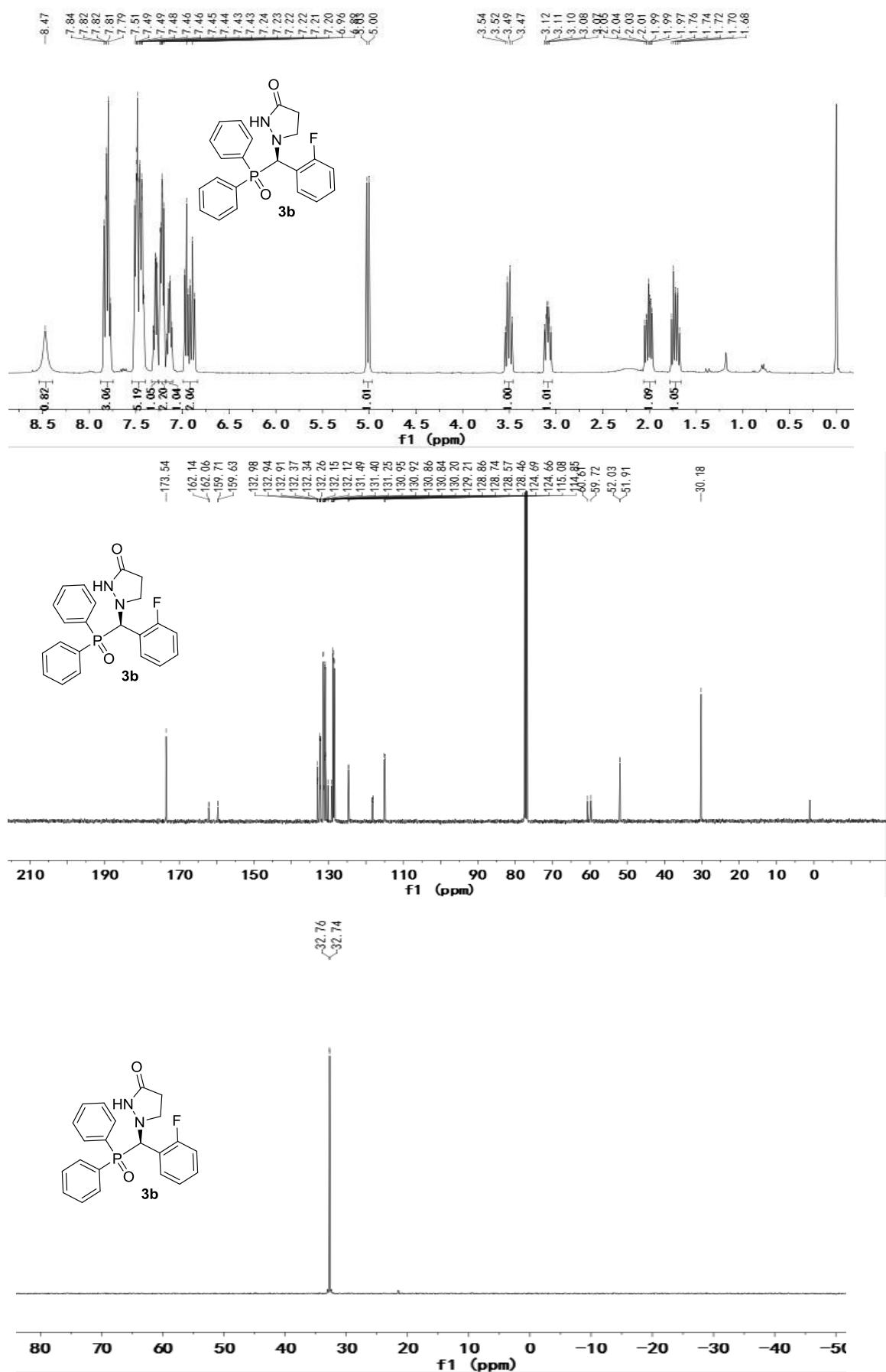


(R)-1-((diphenylphosphoryl)(phenyl)methyl)pyrazolidin-3-one (3a)

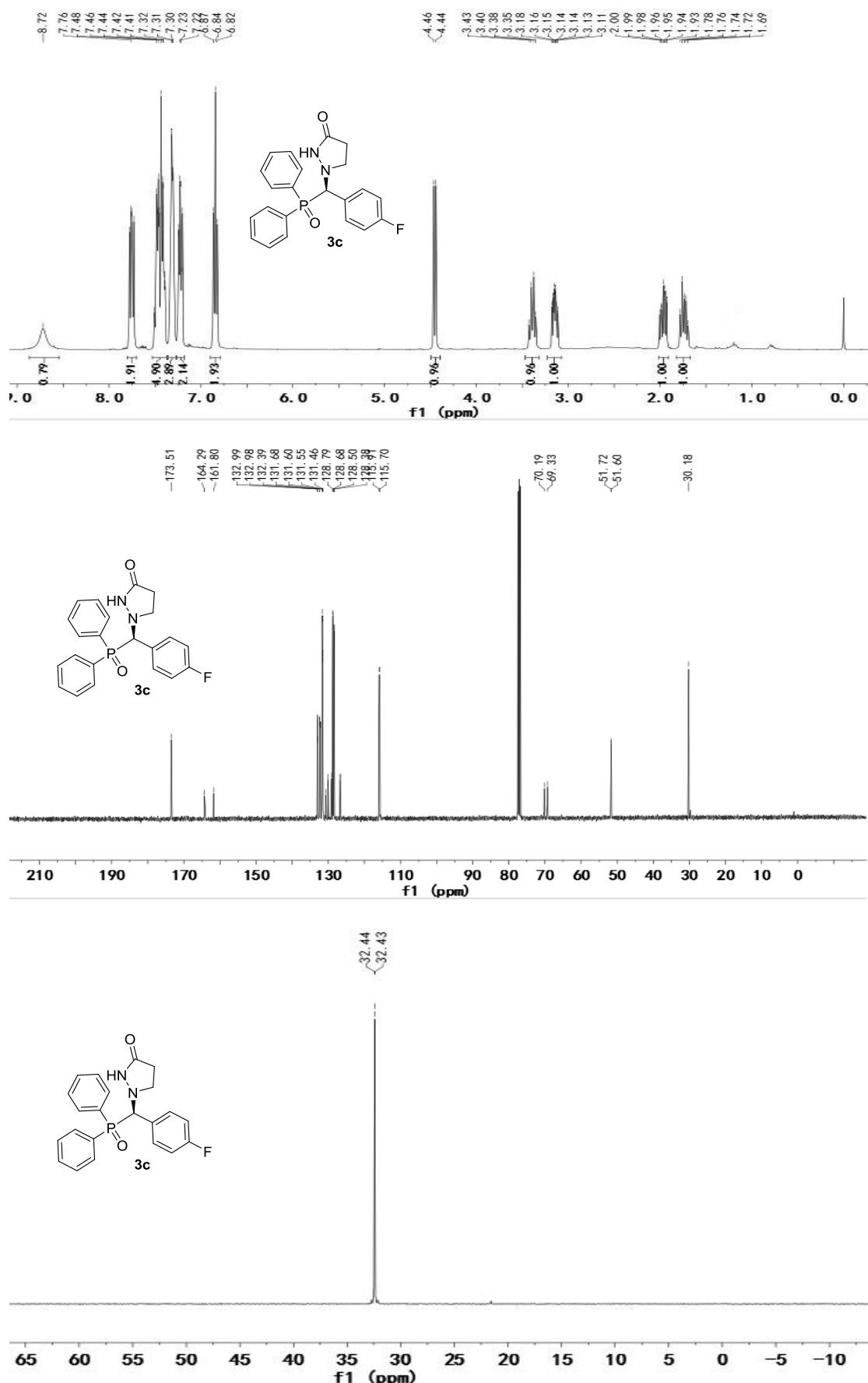




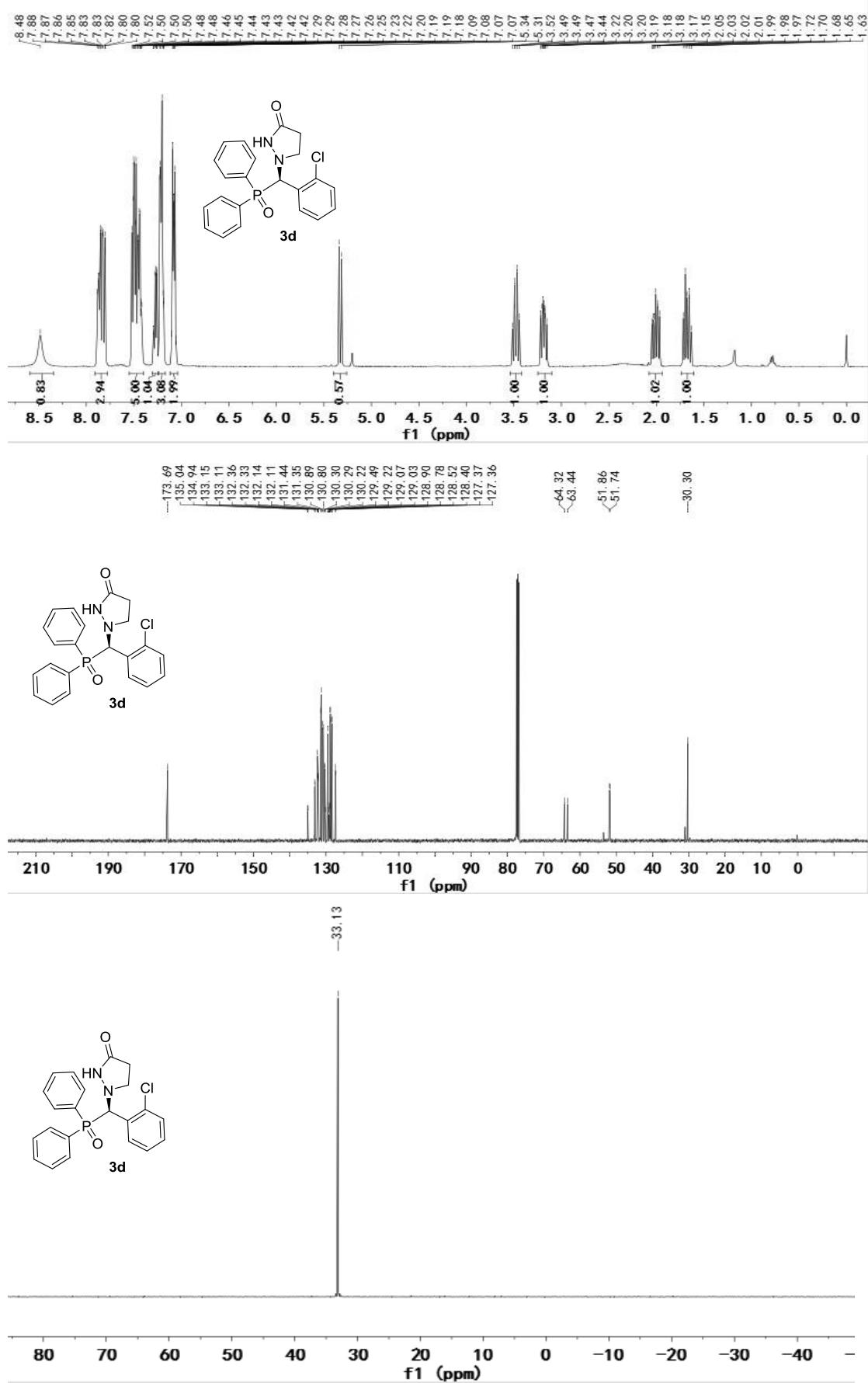
(R)-1-((diphenylphosphoryl)(2-fluorophenyl)methyl)pyrazolidin-3-one (3b)



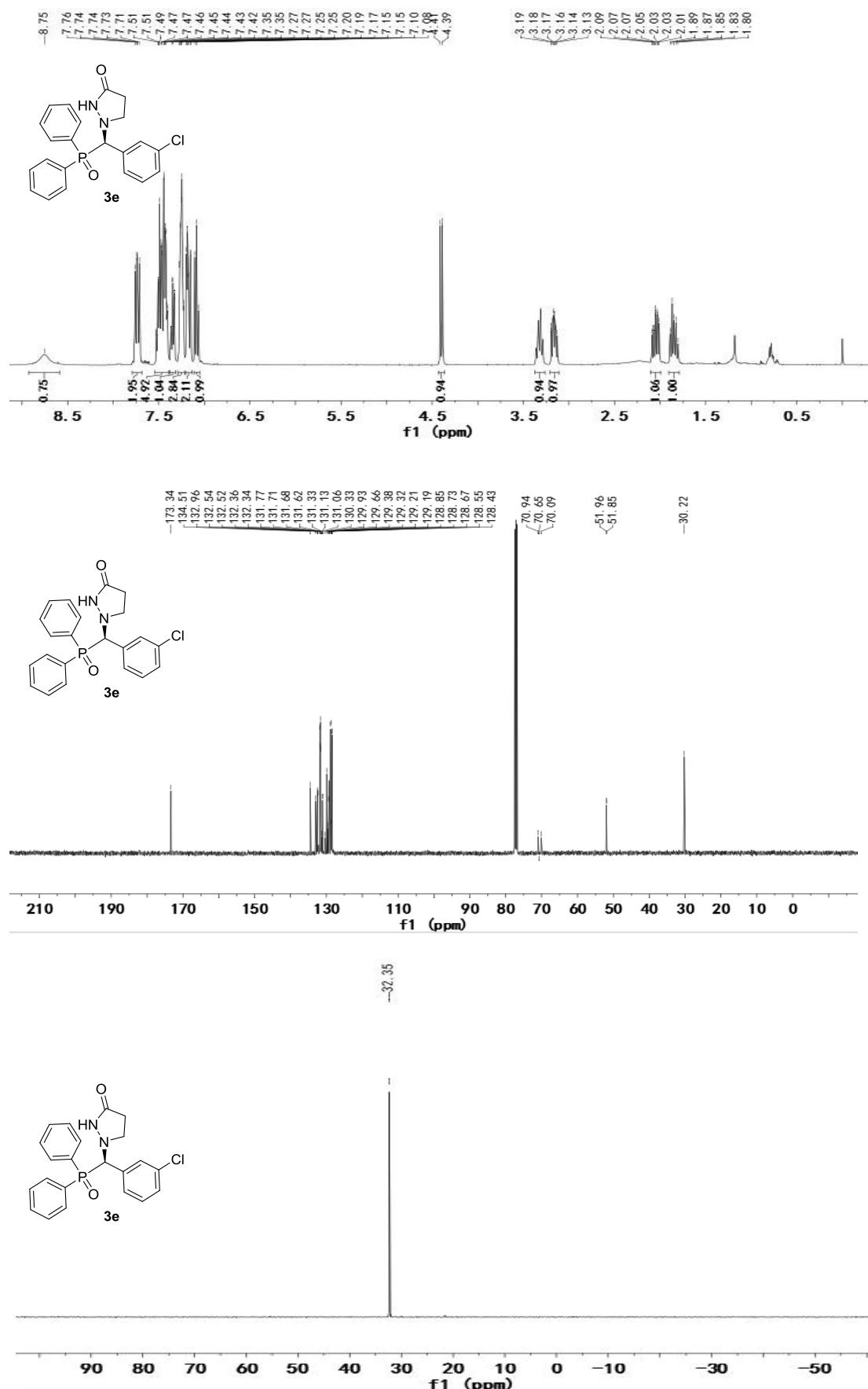
(R)-1-((diphenylphosphoryl)(4-fluorophenyl)methyl)pyrazolidin-3-one (3c)



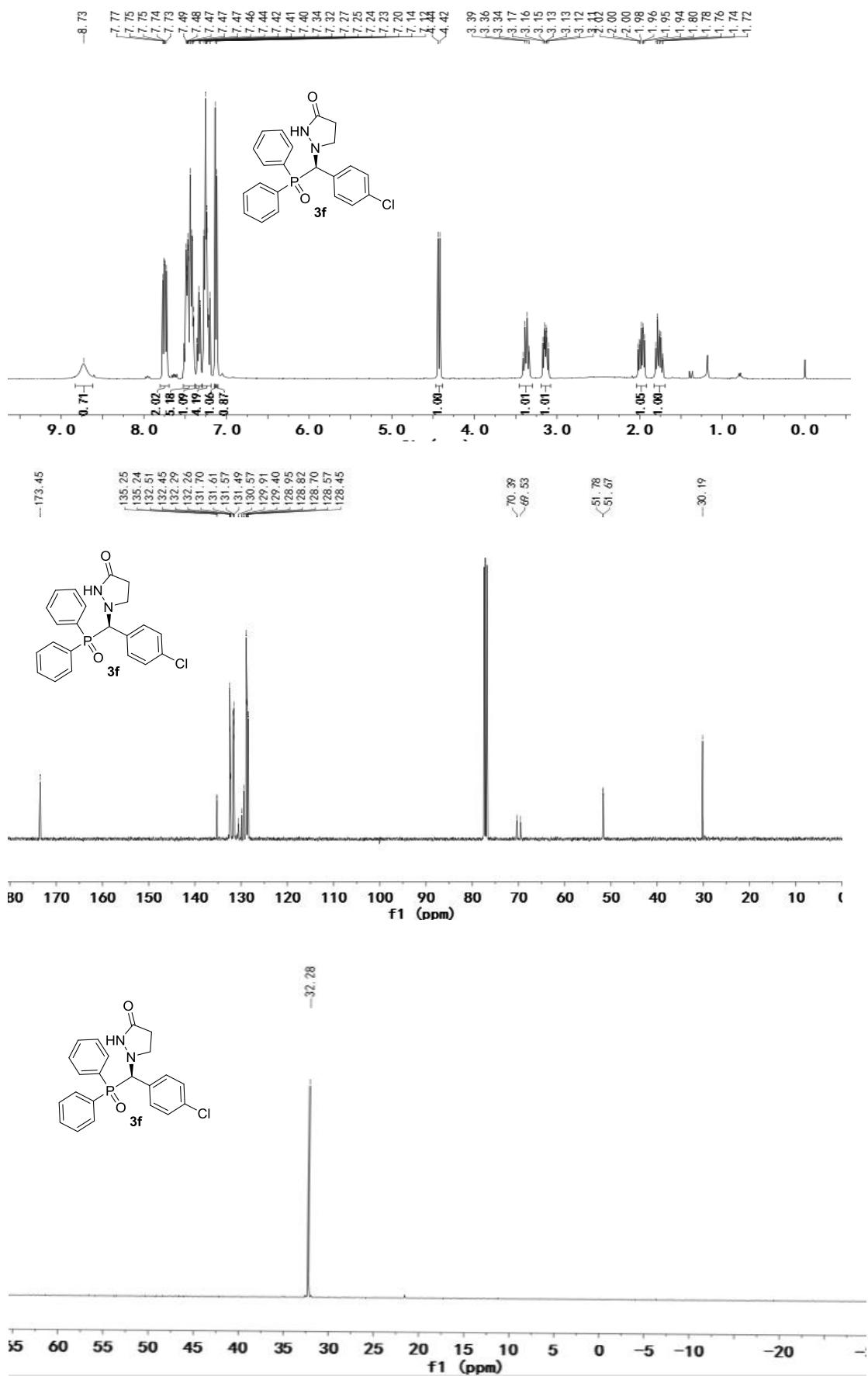
(R)-1-((2-chlorophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3d)



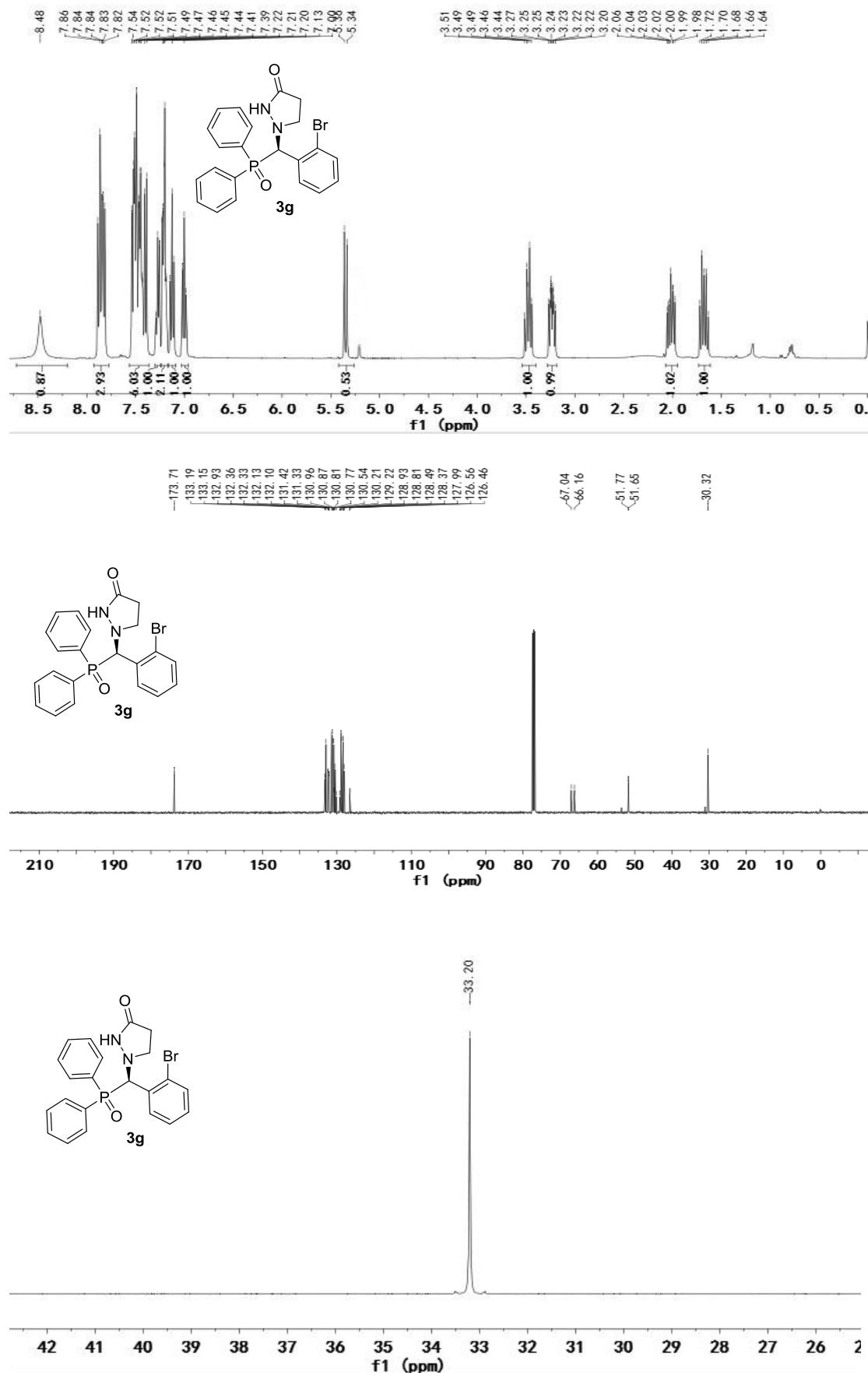
(R)-1-((3-chlorophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3e)



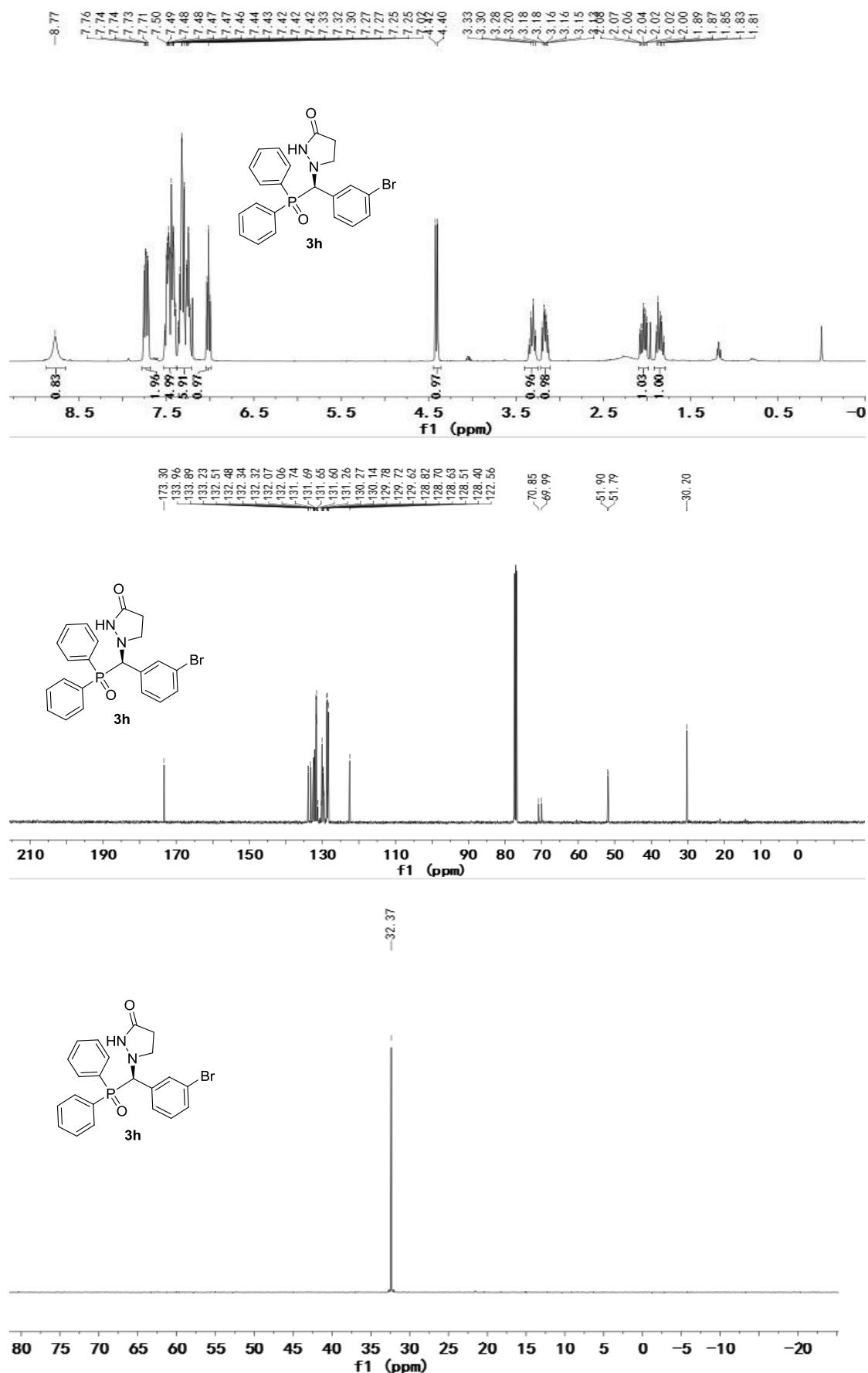
(R)-1-((4-chlorophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3f)



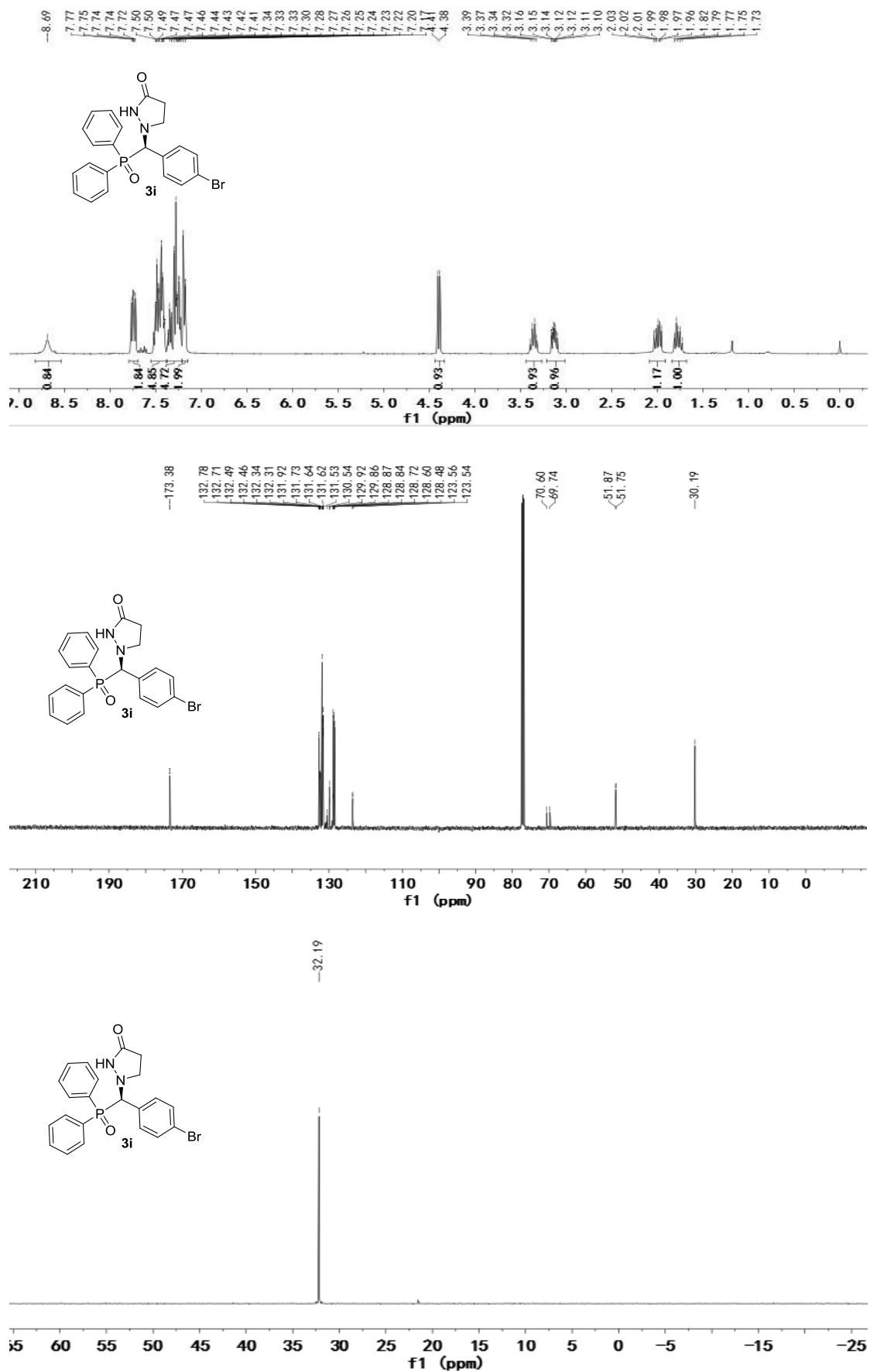
(R)-1-((2-bromophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3g)



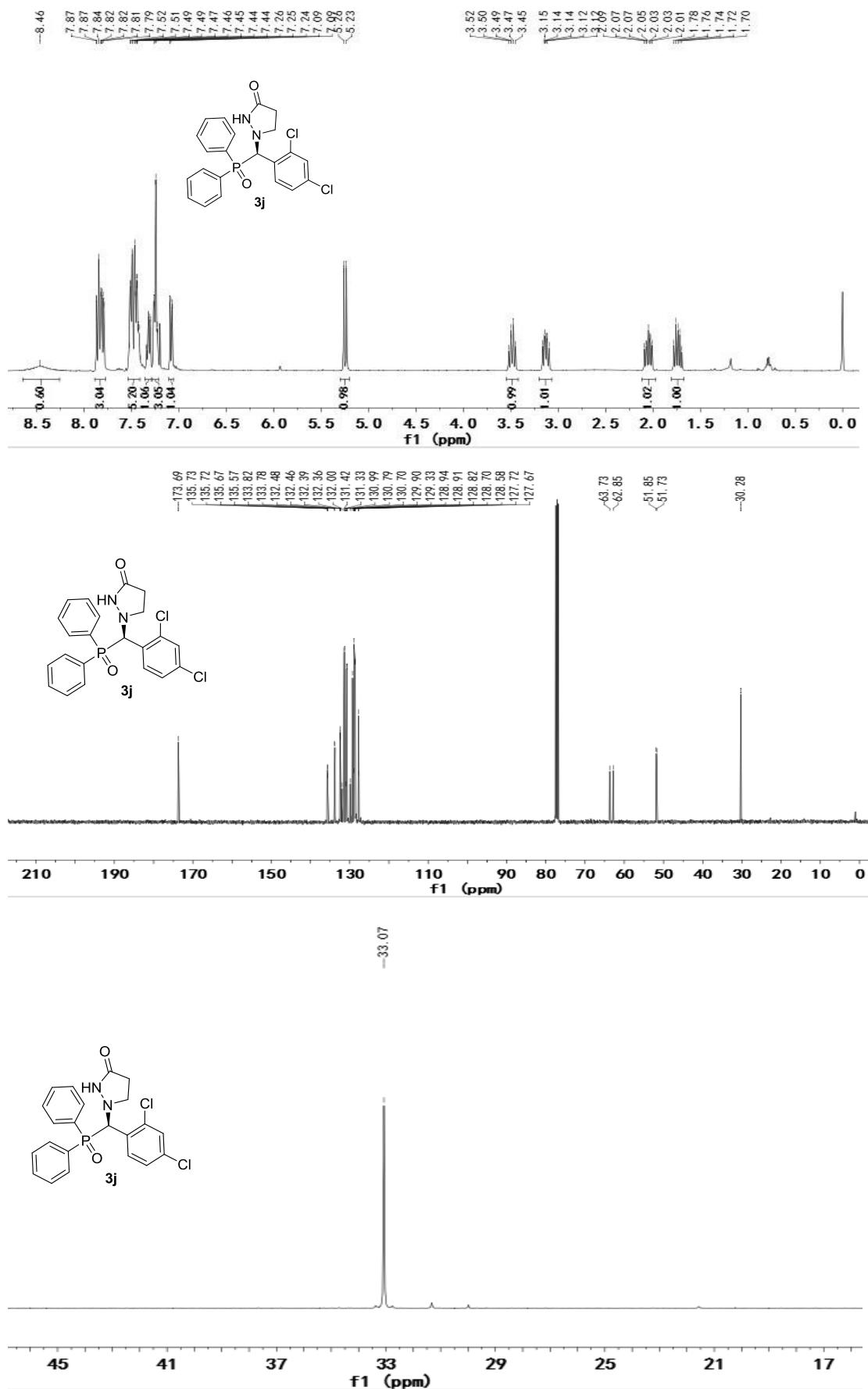
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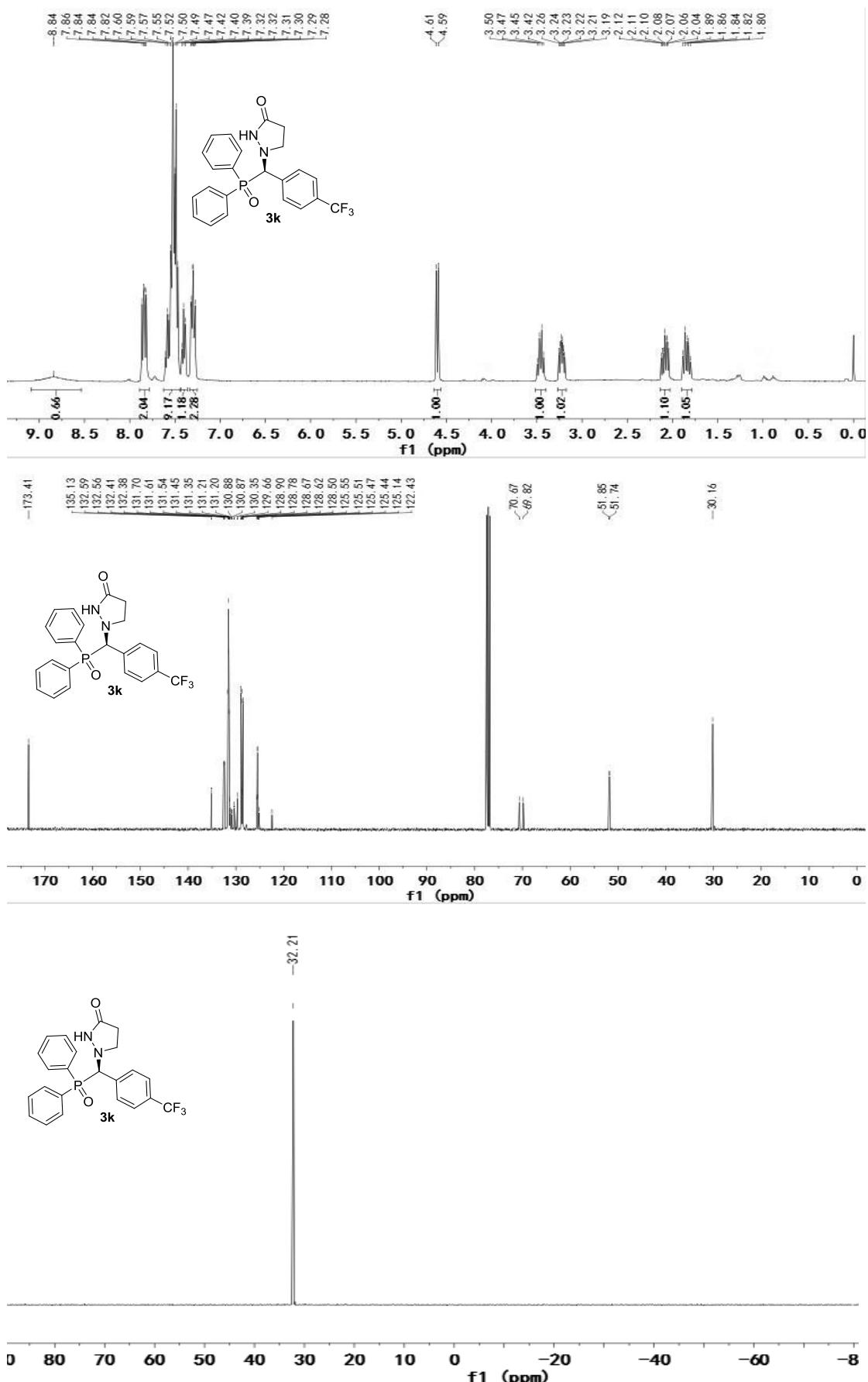
(R)-1-((4-bromophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3i)



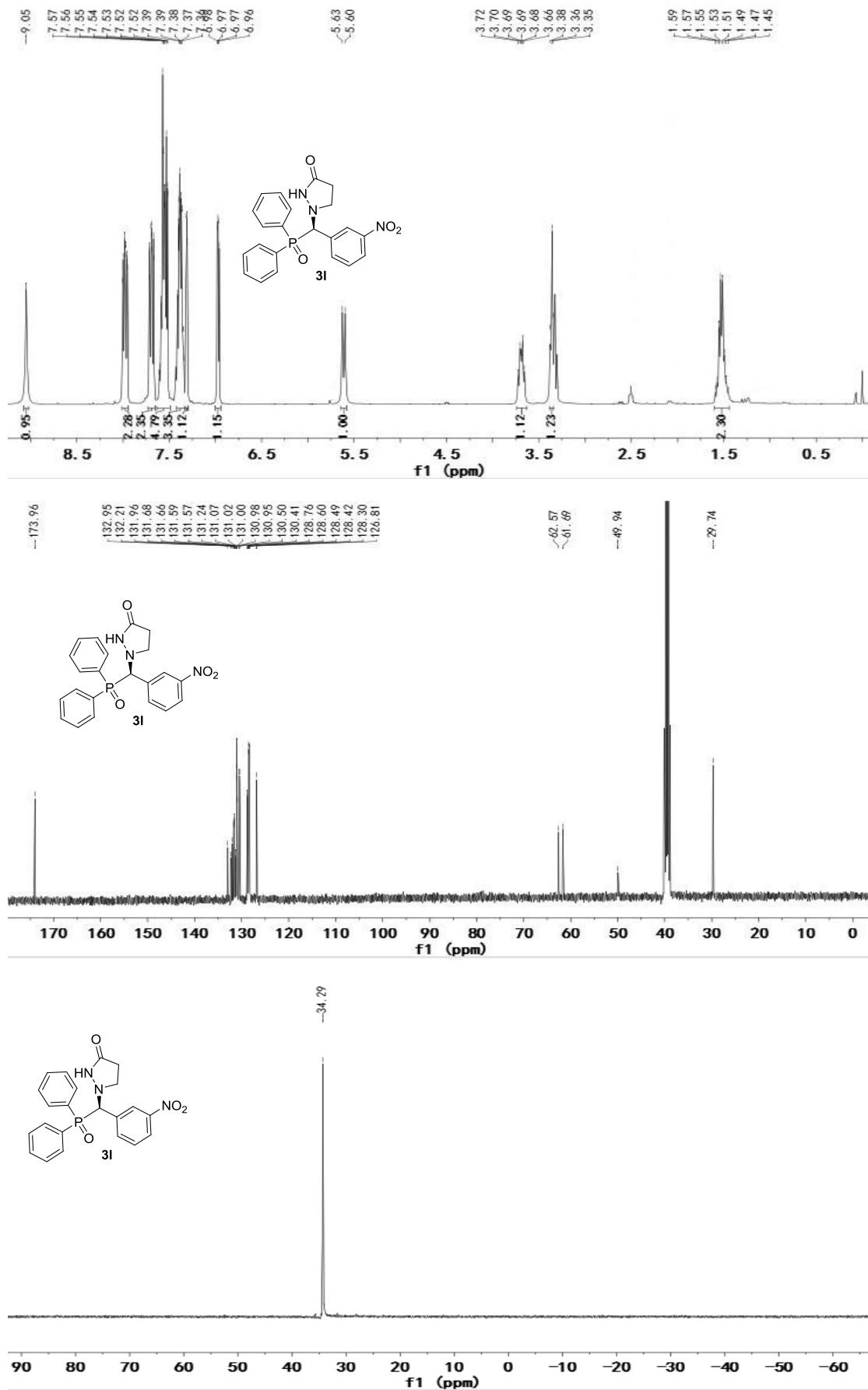
(R)-1-((2,4-dichlorophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3j)



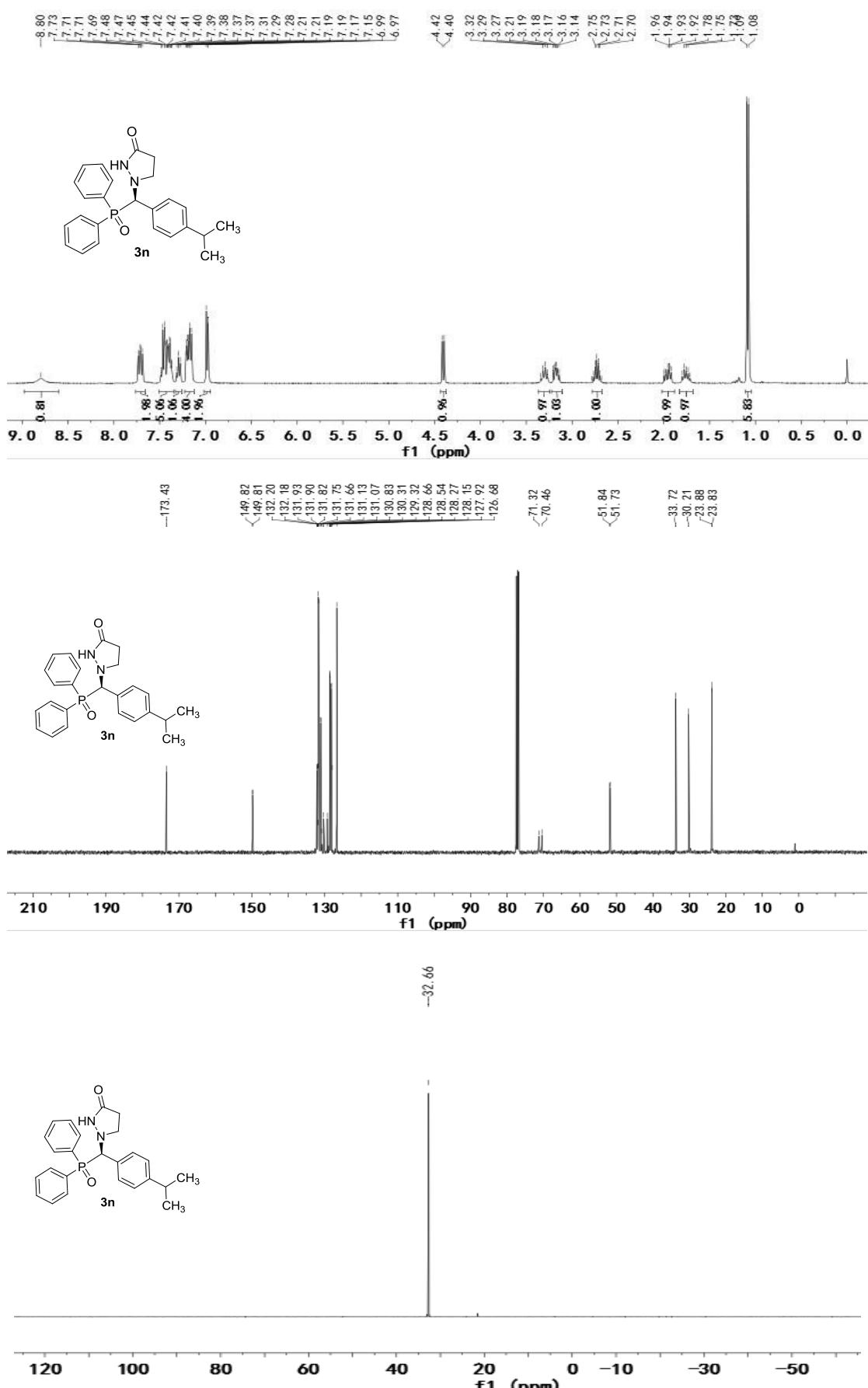
(R)-1-((diphenylphosphoryl)(4-(trifluoromethyl)phenyl)methyl)pyrazolidin-3-one (3k)



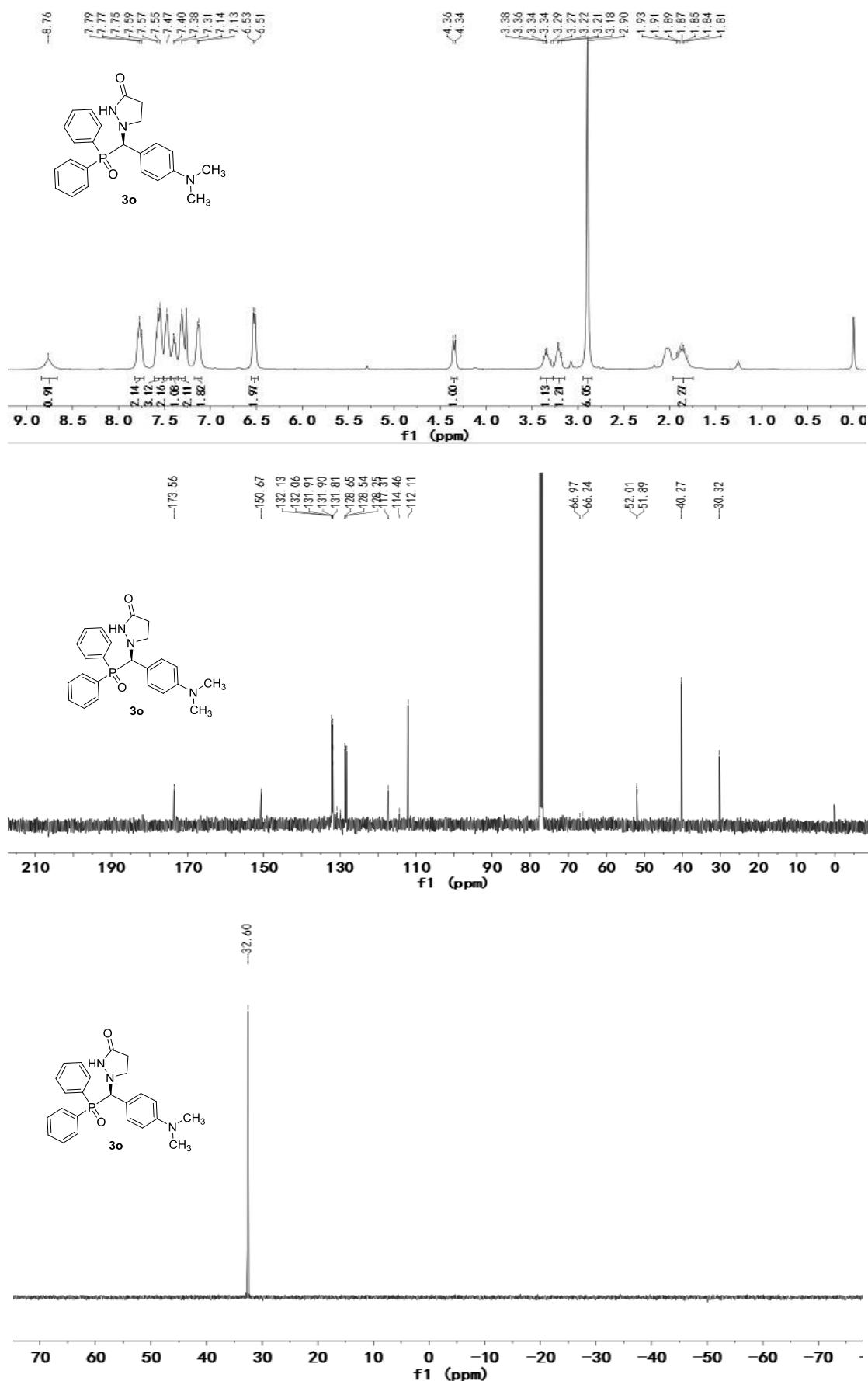
(R)-1-((diphenylphosphoryl)(3-nitrophenyl)methyl)pyrazolidin-3-one (3l)



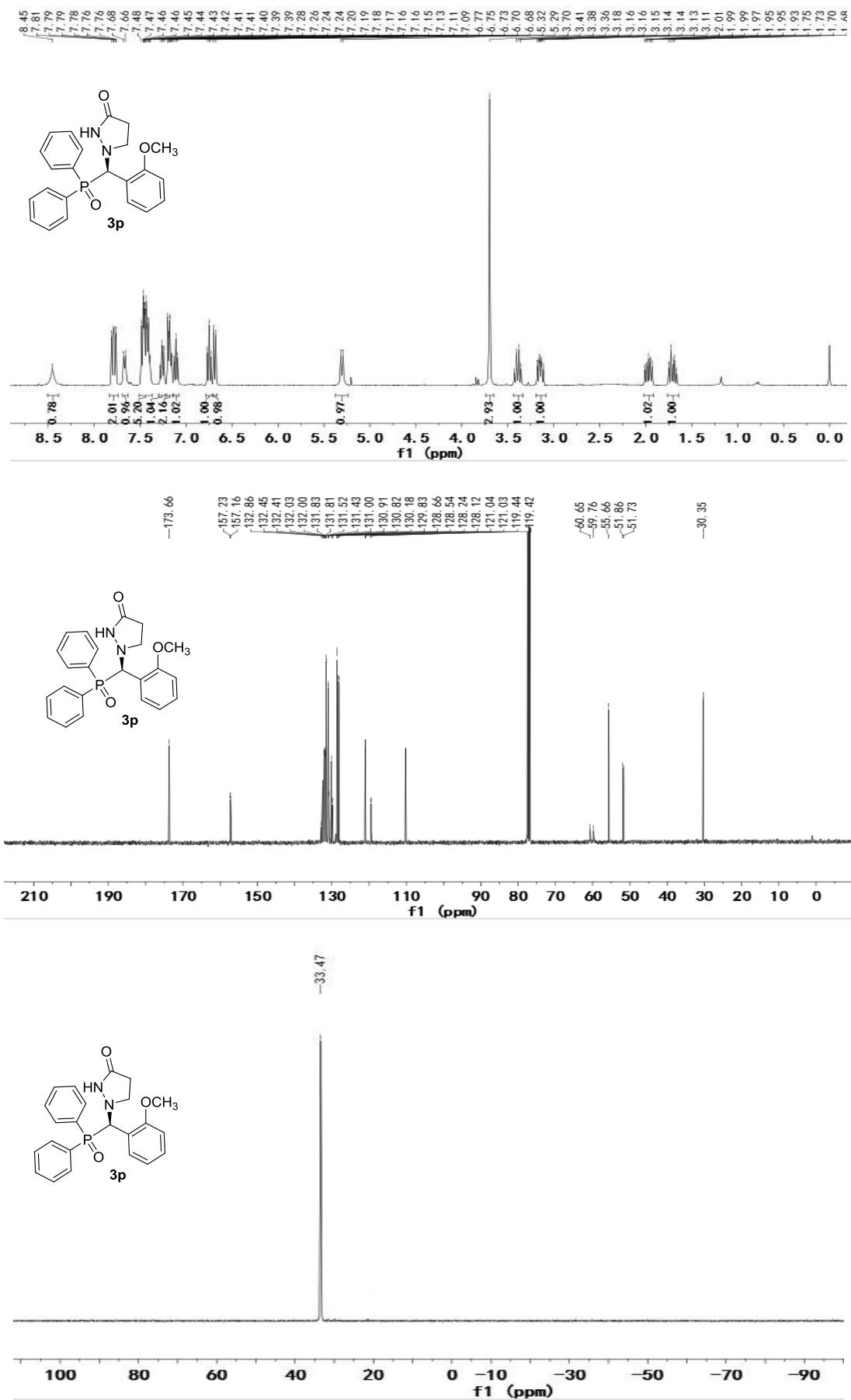
(R)-1-((diphenylphosphoryl)(4-isopropylphenyl)methyl)pyrazolidin-3-one (3n)



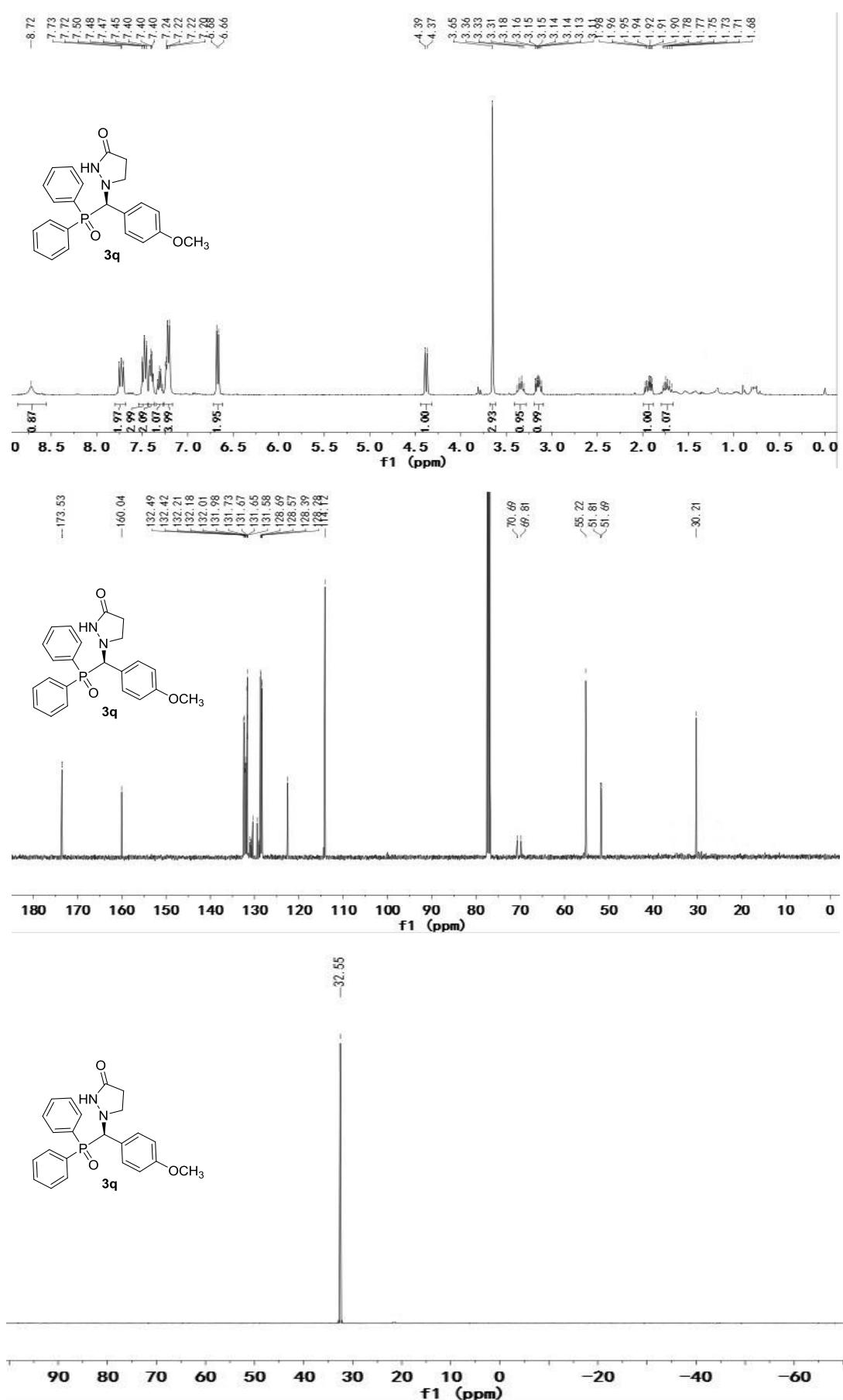
(R)-1-((4-(dimethylamino)phenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3o)



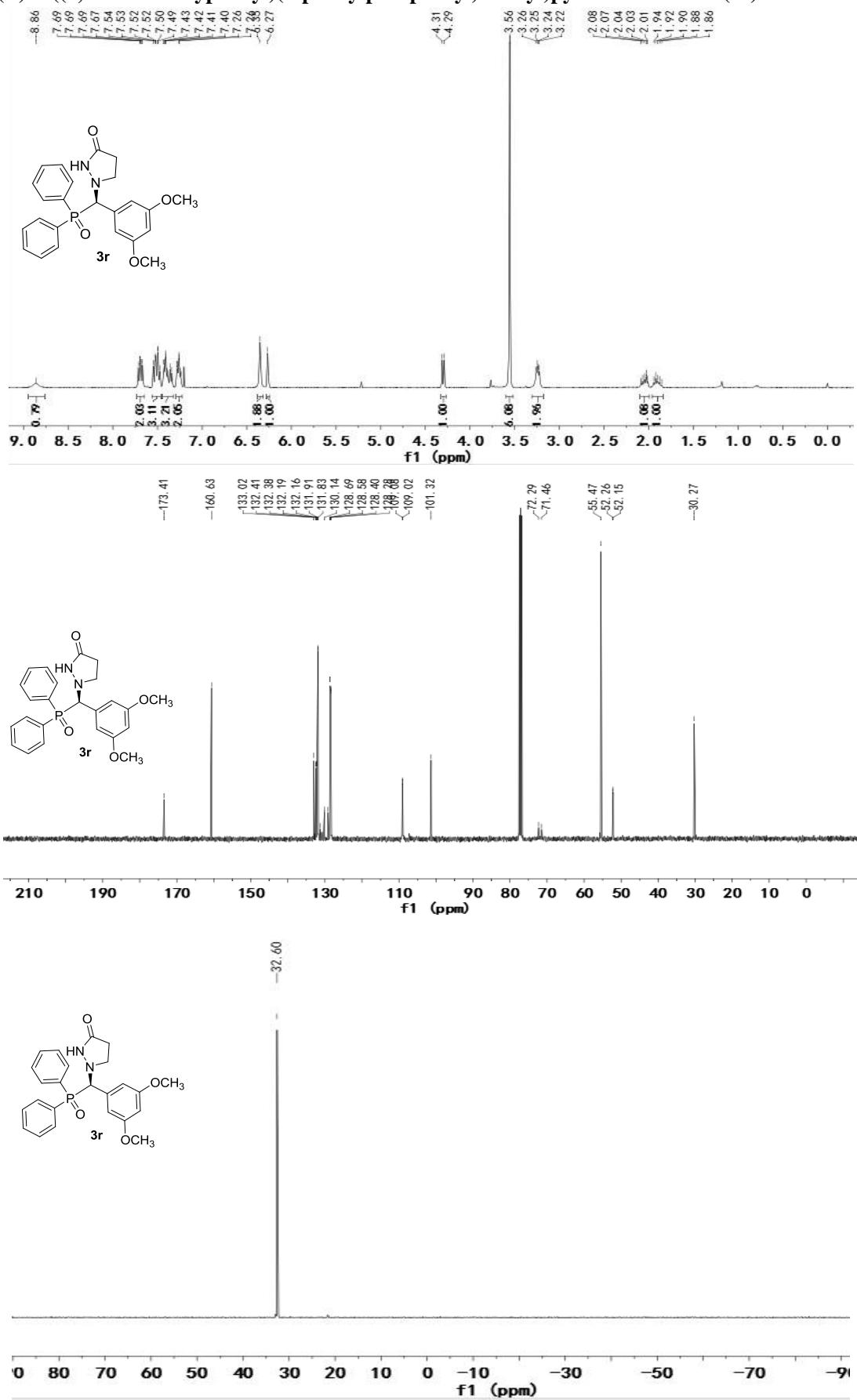
(R)-1-((diphenylphosphoryl)(2-methoxyphenyl)methyl)pyrazolidin-3-one (3p)



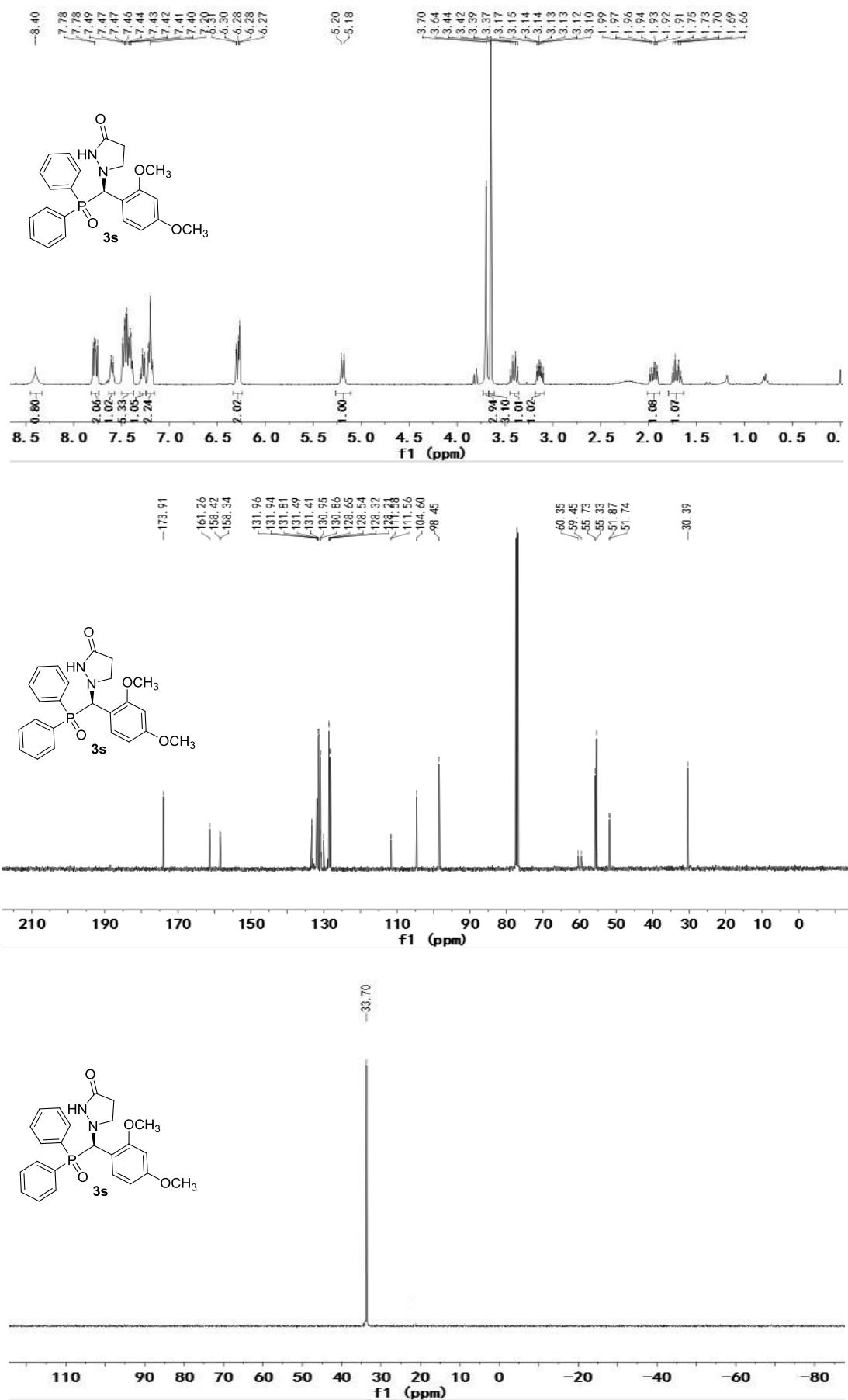
(R)-1-((diphenylphosphoryl)(4-methoxyphenyl)methyl)pyrazolidin-3-one (3q)



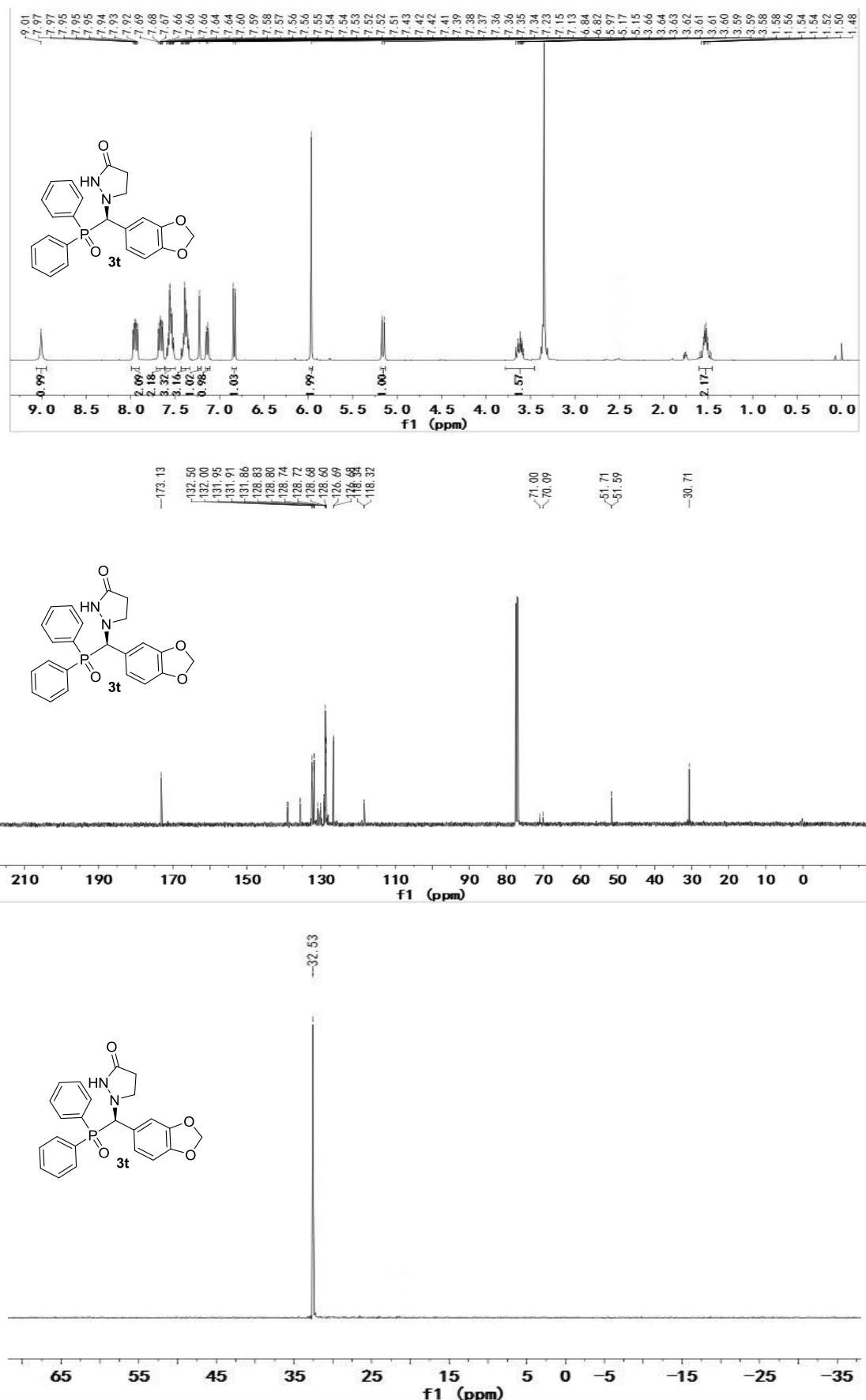
(R)-1-((3, 5-dimethoxyphenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3r)



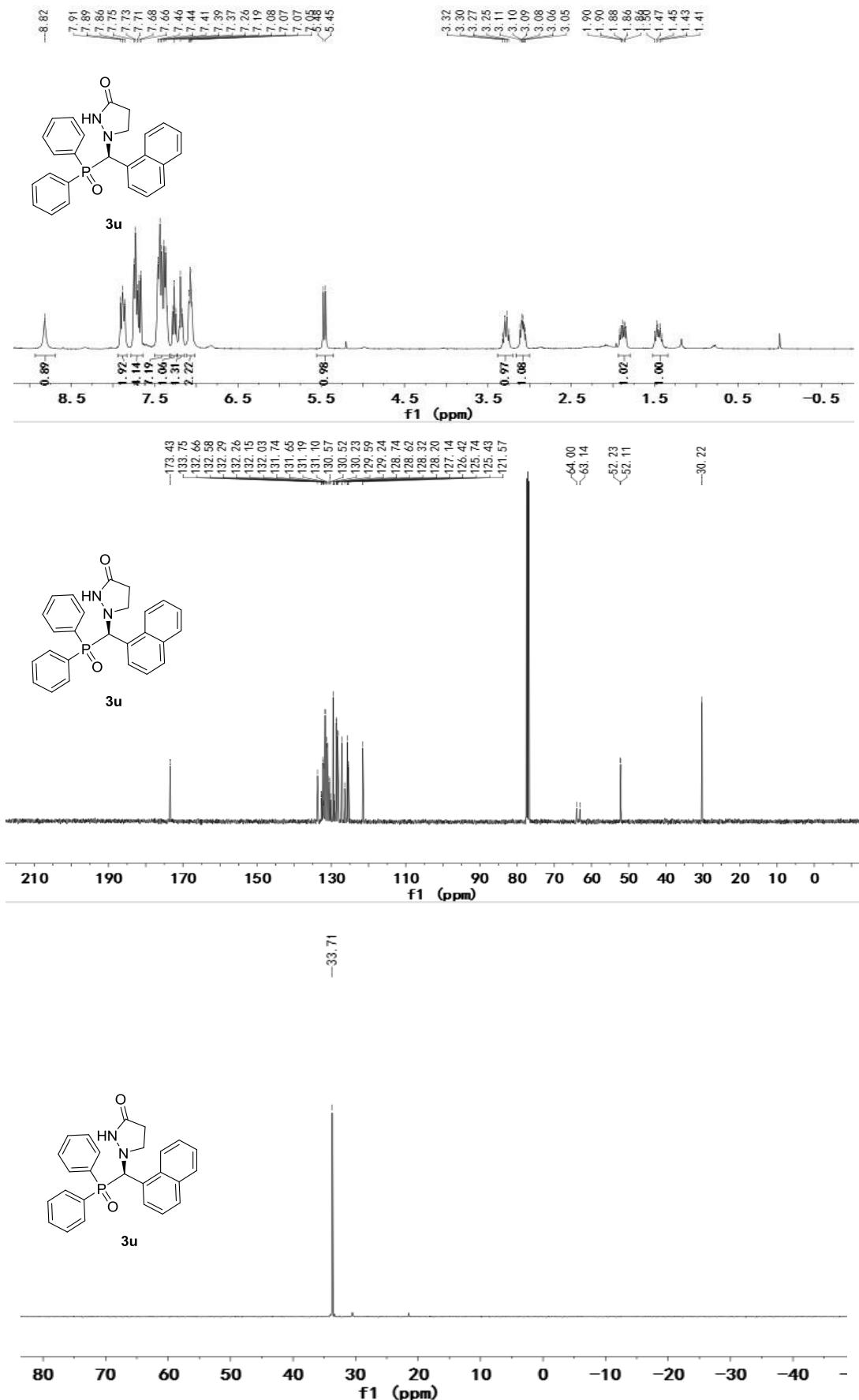
(R)-1-((2, 4-dimethoxyphenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3s)



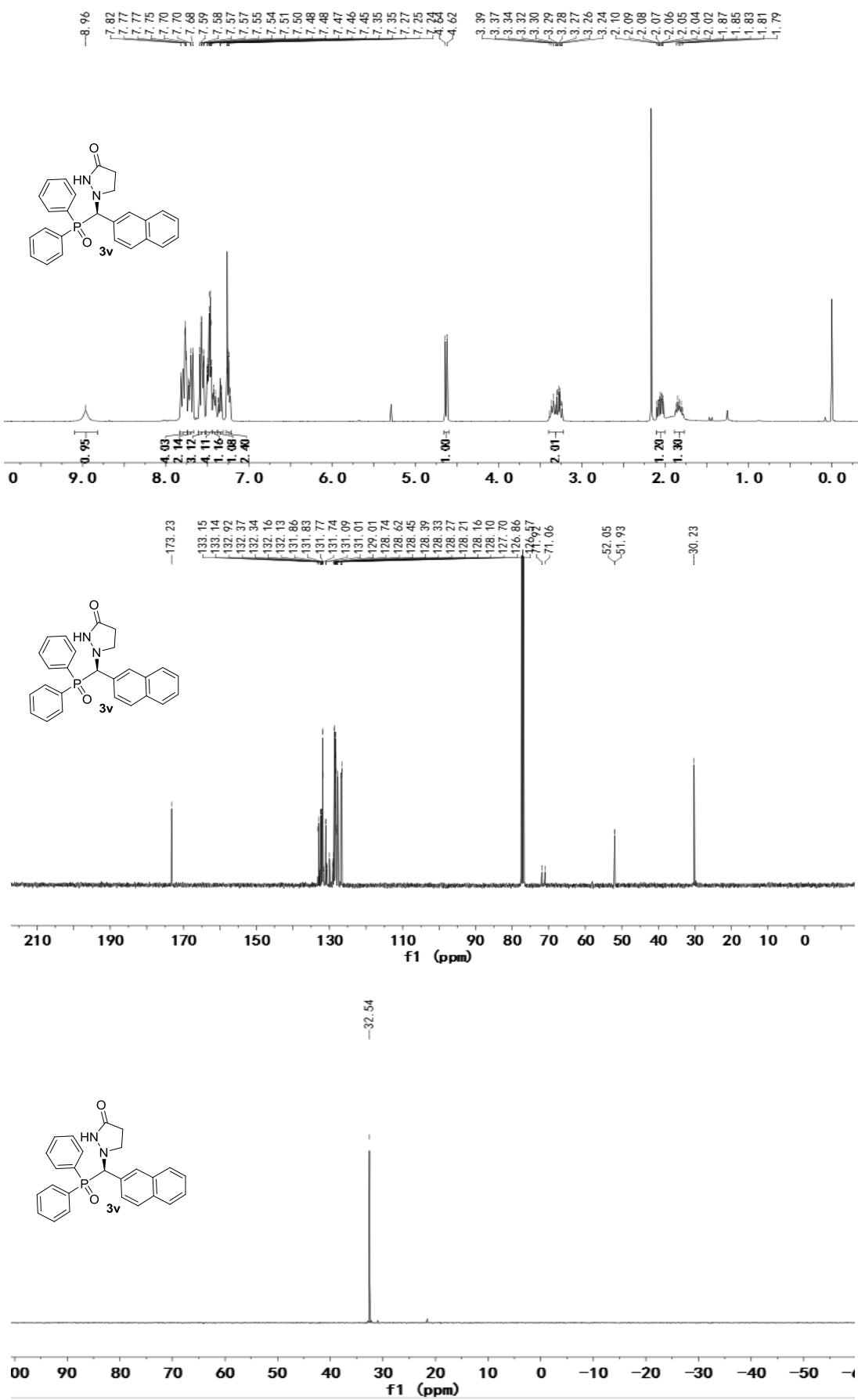
(R)-1-(benzo[d][1,3]dioxol-5-yl(diphenylphosphoryl)methyl)pyrazolidin-3-one (3t)



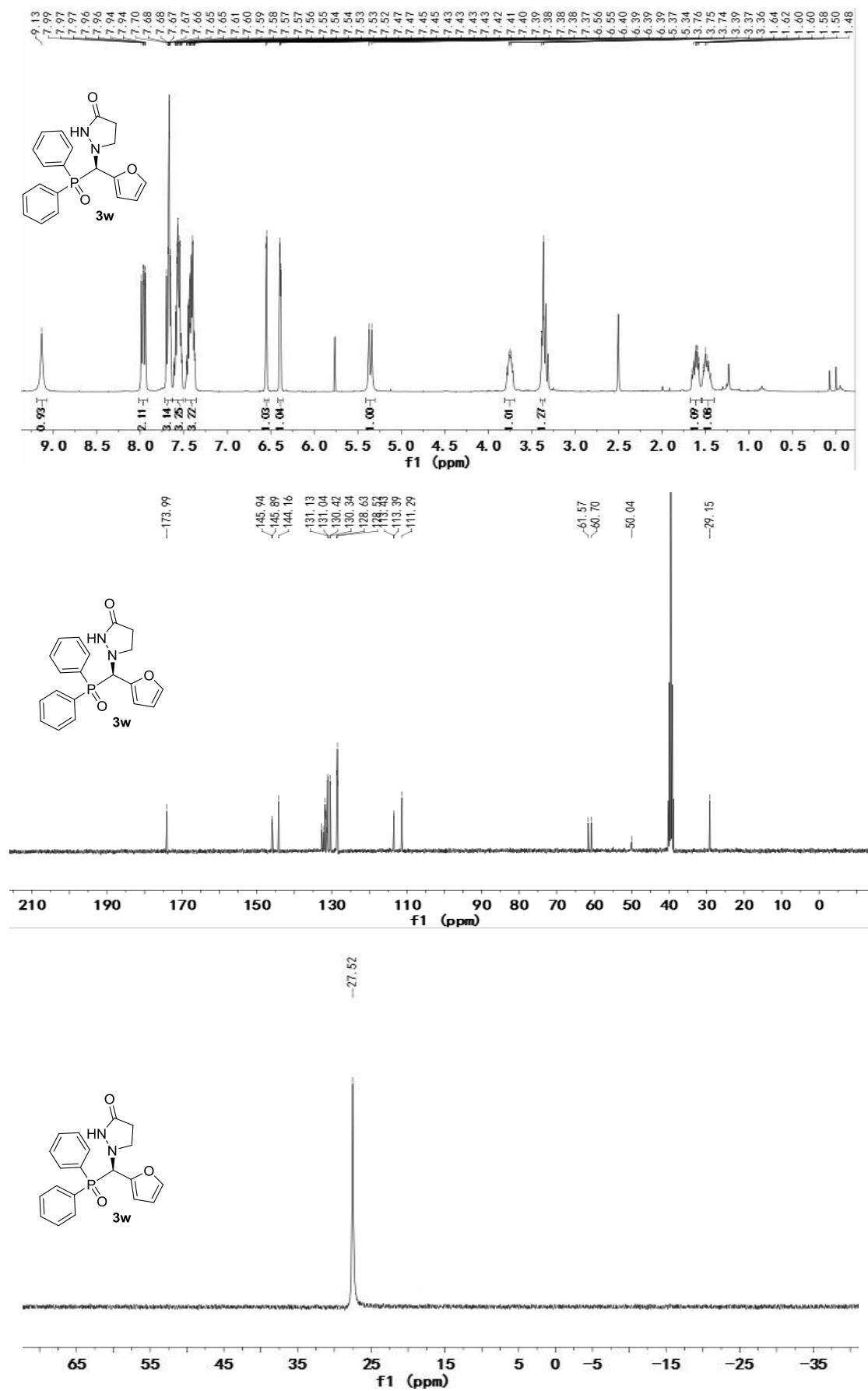
(R)-1-((diphenylphosphoryl)(naphthalen-1-yl)methyl)pyrazolidin-3-one (3u)



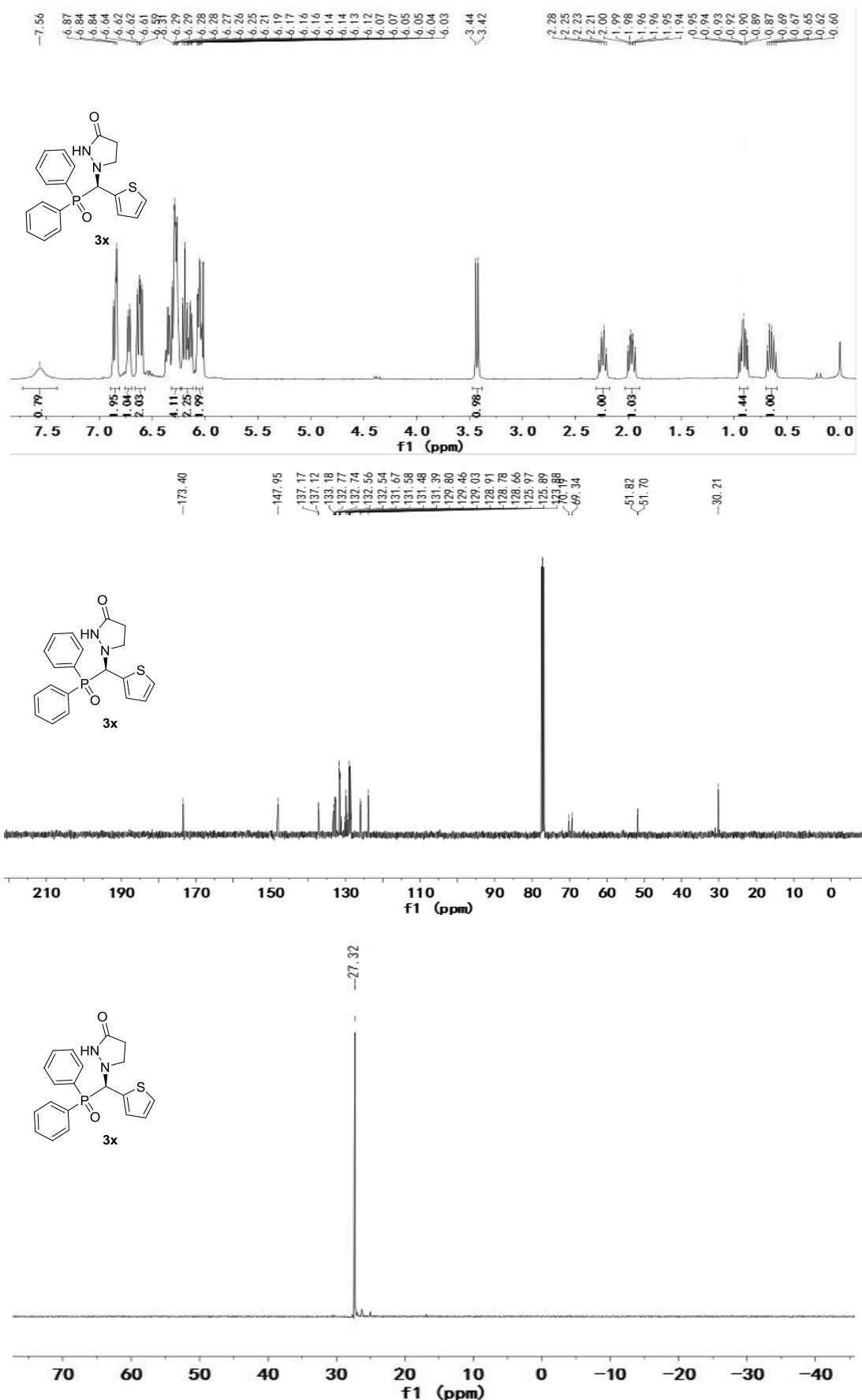
(R)-1-((diphenylphosphoryl)(naphthalen-2-yl)methyl)pyrazolidin-3-one (3v)



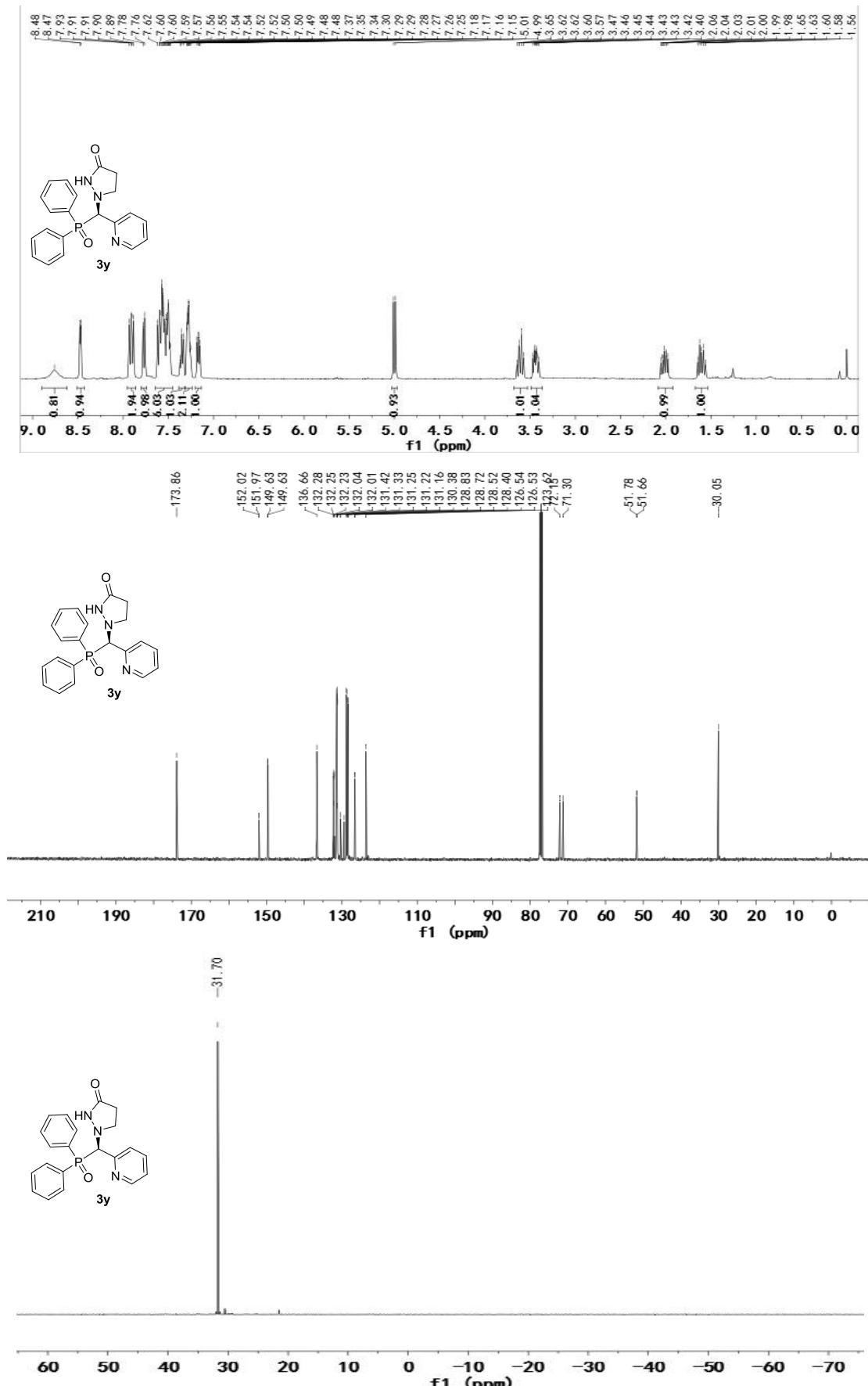
(R)-1-((diphenylphosphoryl)(furan-3-yl)methyl)pyrazolidin-3-one (3w)



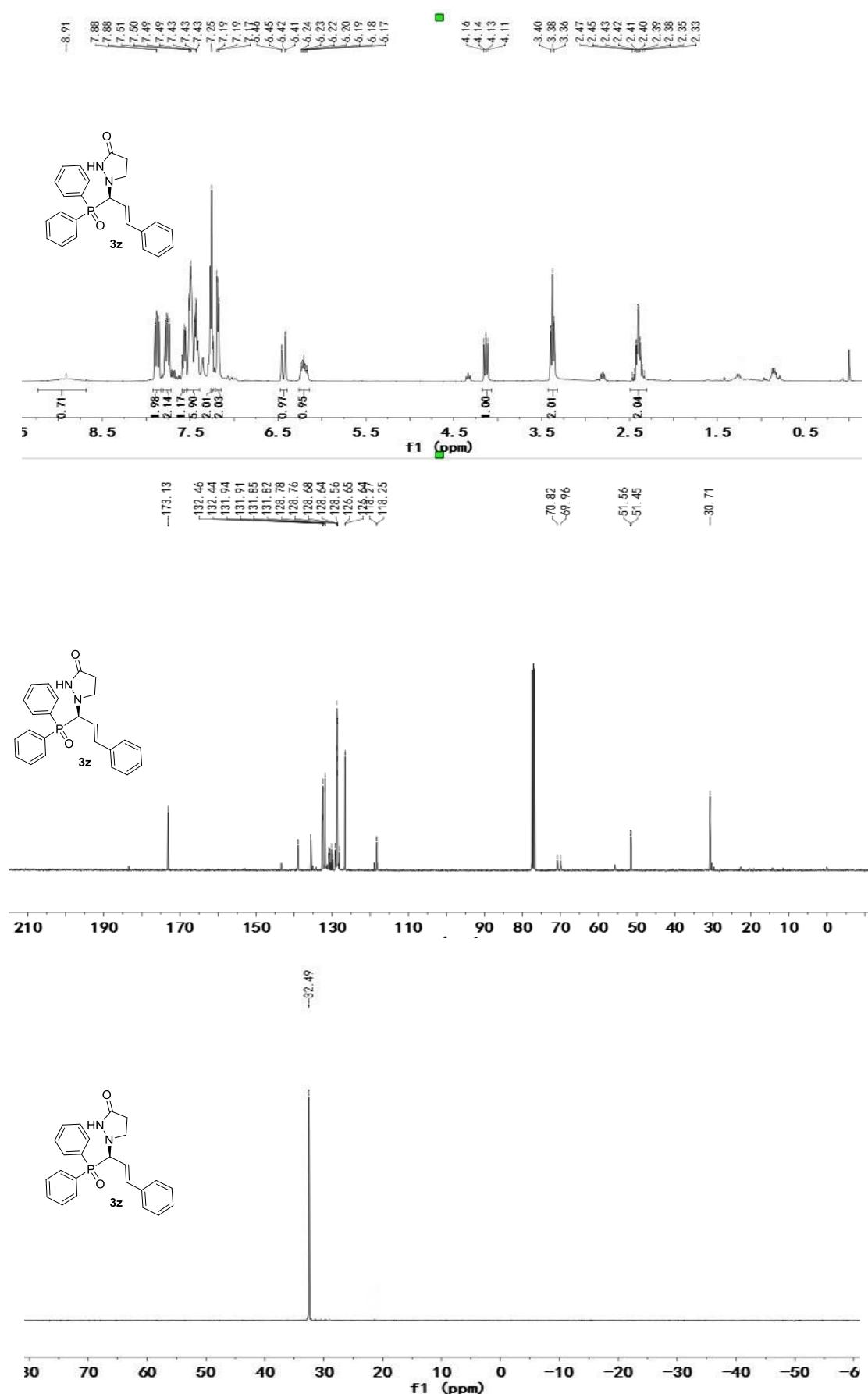
(R)-1-((diphenylphosphoryl)(thiophen-2-yl)methyl)pyrazolidin-3-one (3x)



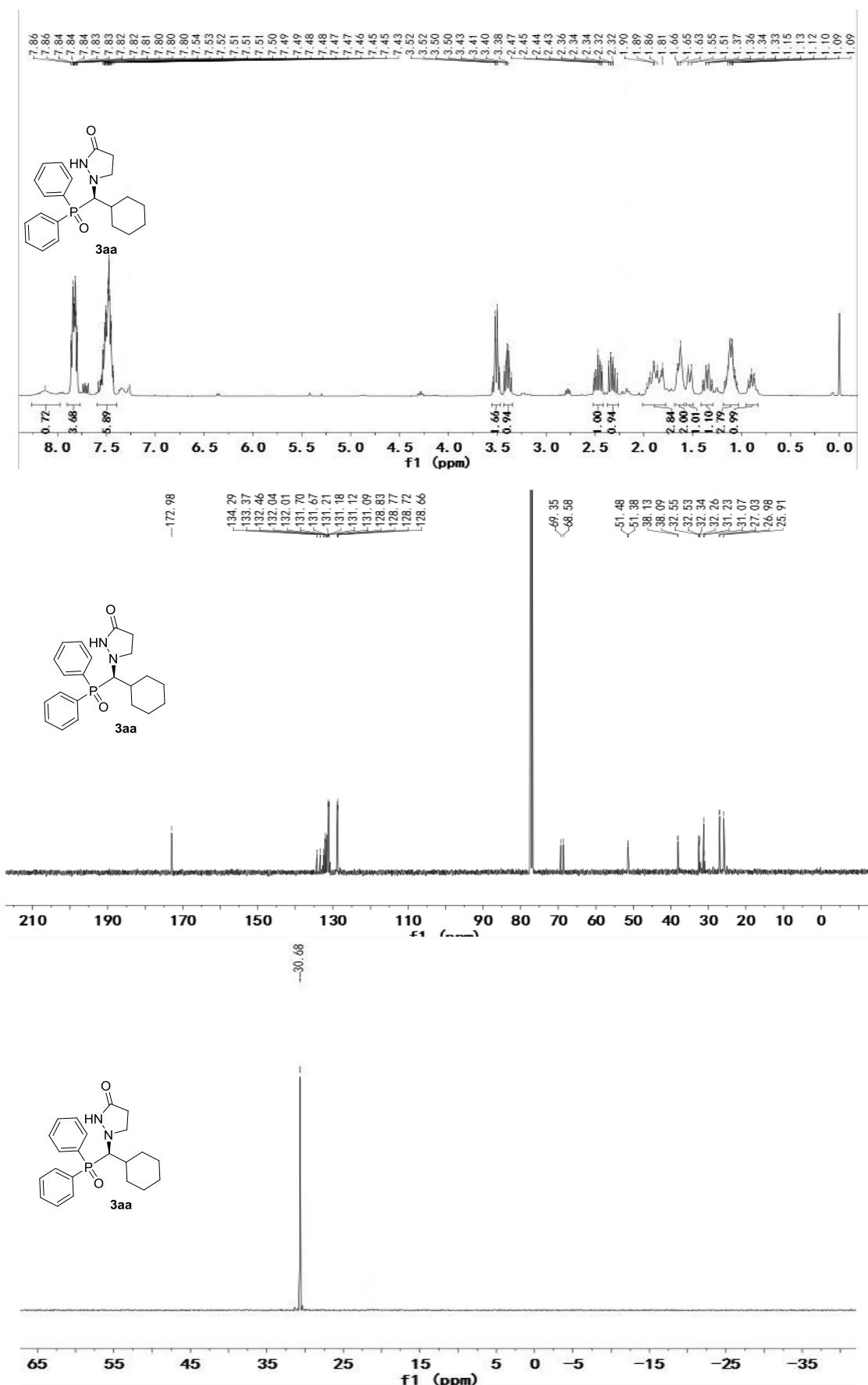
(R)-1-((diphenylphosphoryl)(pyridin-2-yl)methyl)pyrazolidin-3-one (3y)



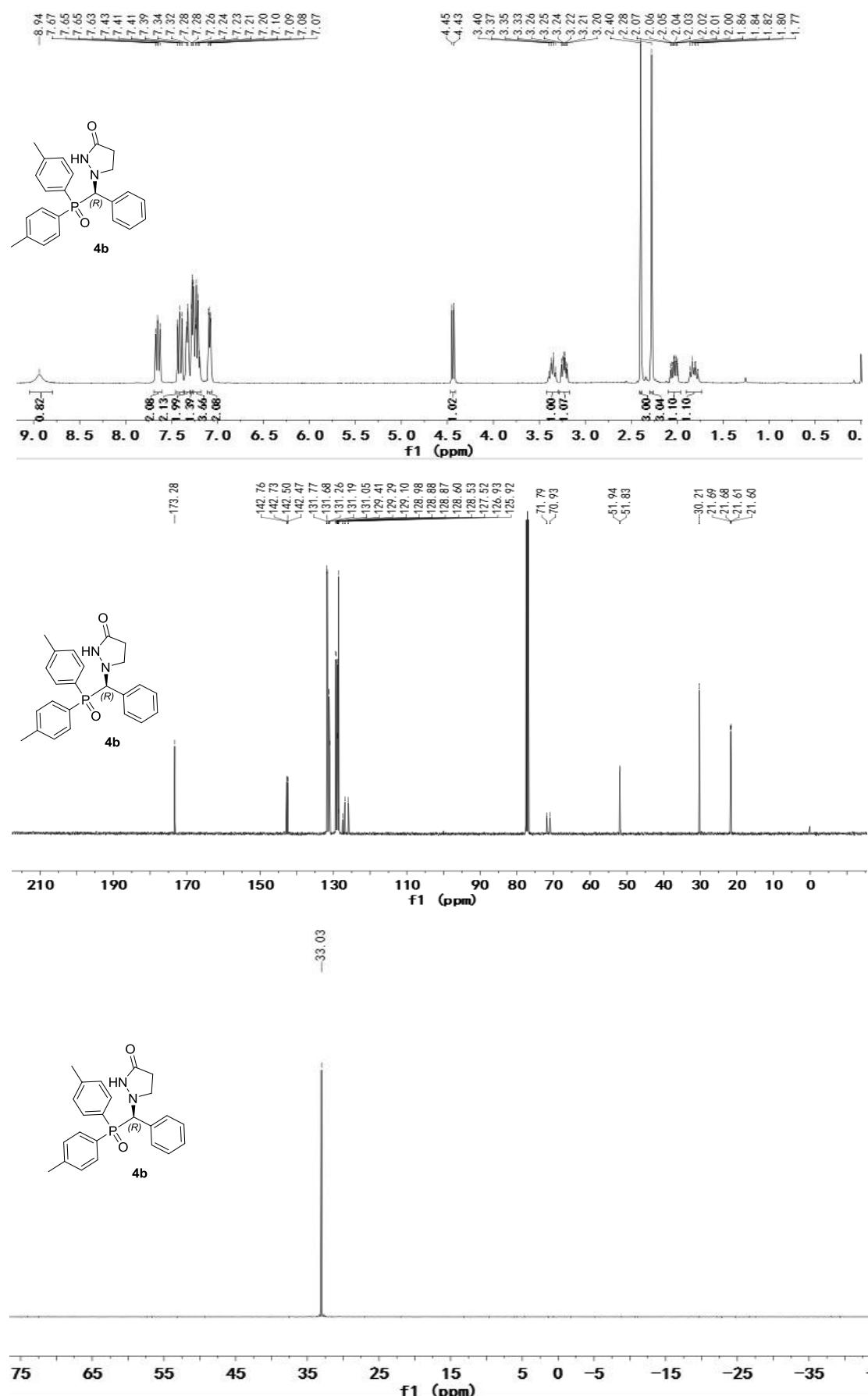
(*R,E*)-1-(1-(diphenylphosphoryl)-3-phenylallyl)pyrazolidin-3-one (3z**)**



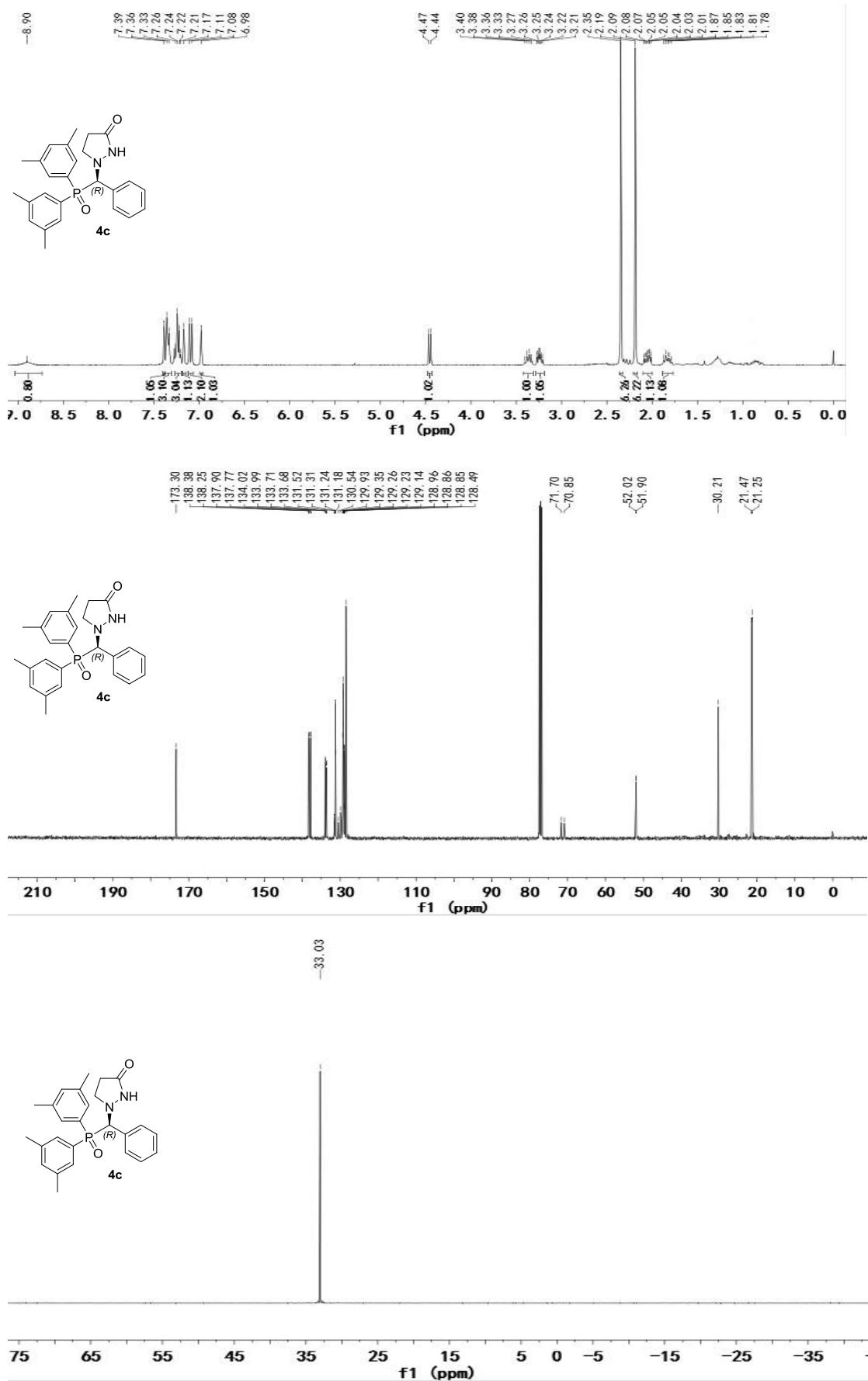
(R)-1-(cyclohexyl(diphenylphosphoryl)methyl)pyrazolidin-3-one (3aa)



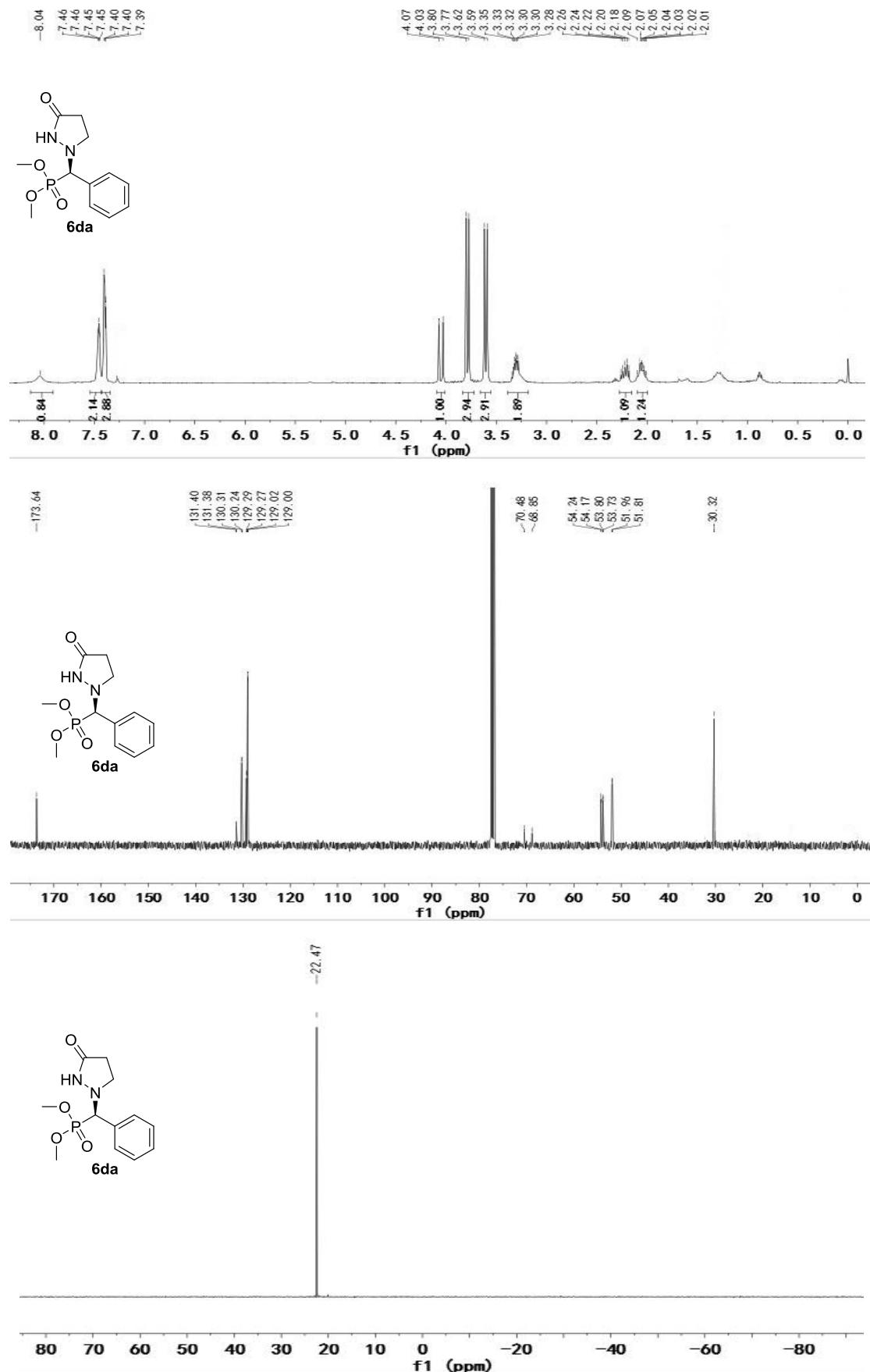
(R)-1-((di-p-tolylphosphoryl)(phenyl)methyl)pyrazolidin-3-one (4b)



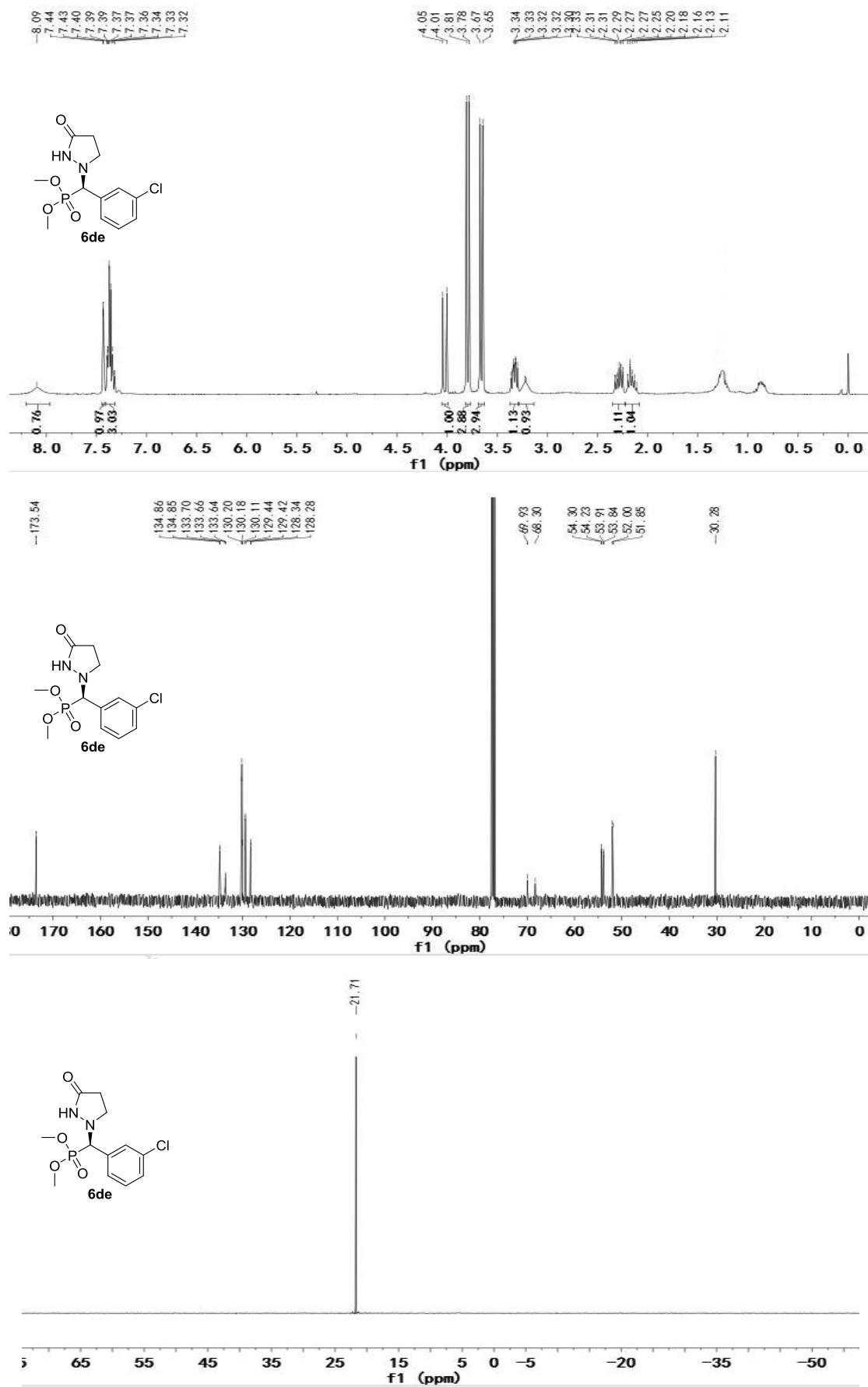
(R)-1-((bis(3,5-dimethylphenyl)phosphoryl)(phenyl)methyl)pyrazolidin-3-one (4c)



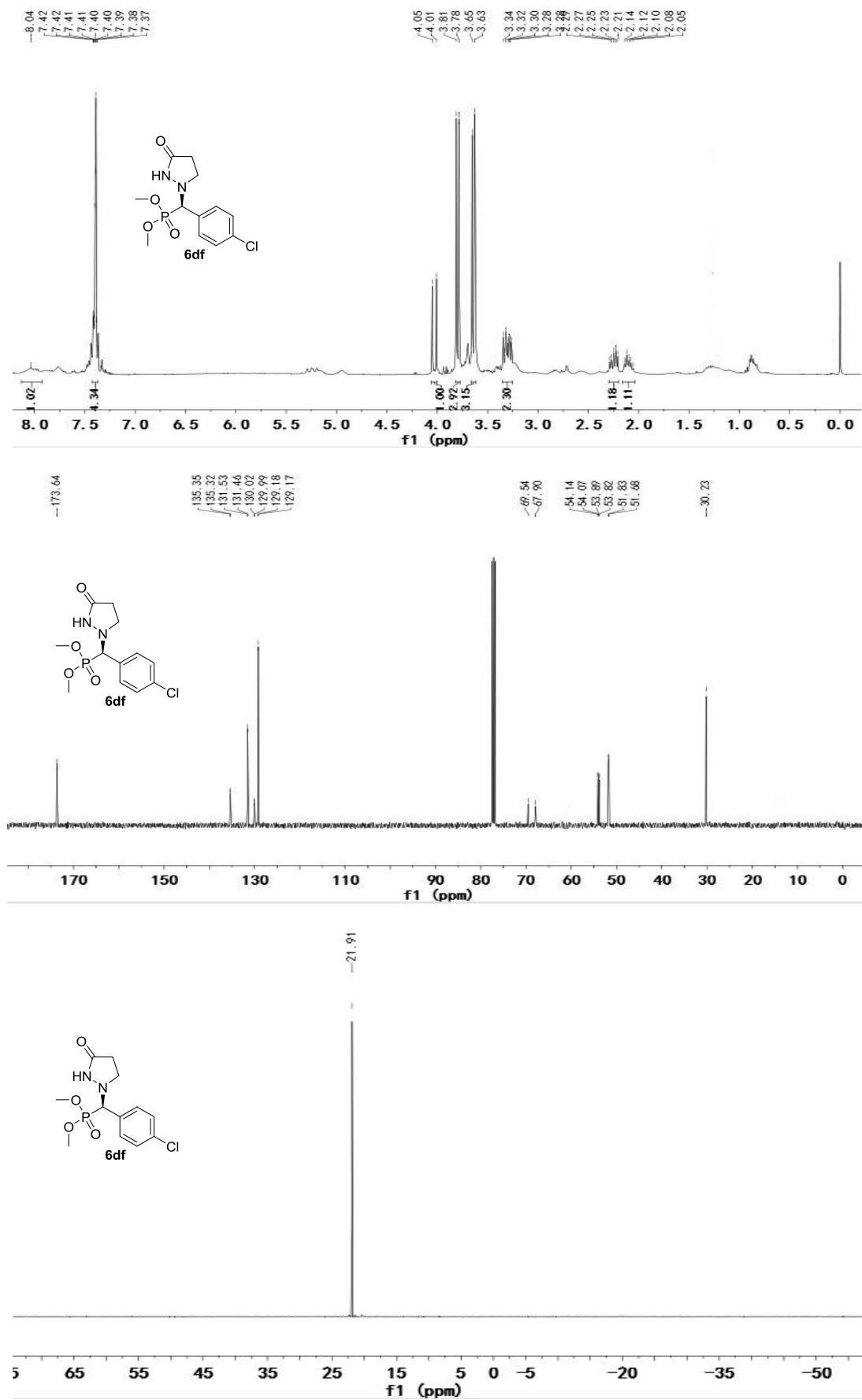
dimethyl (*R*)-((3-oxopyrazolidin-1-yl)(phenyl)methyl)phosphonate (6da)



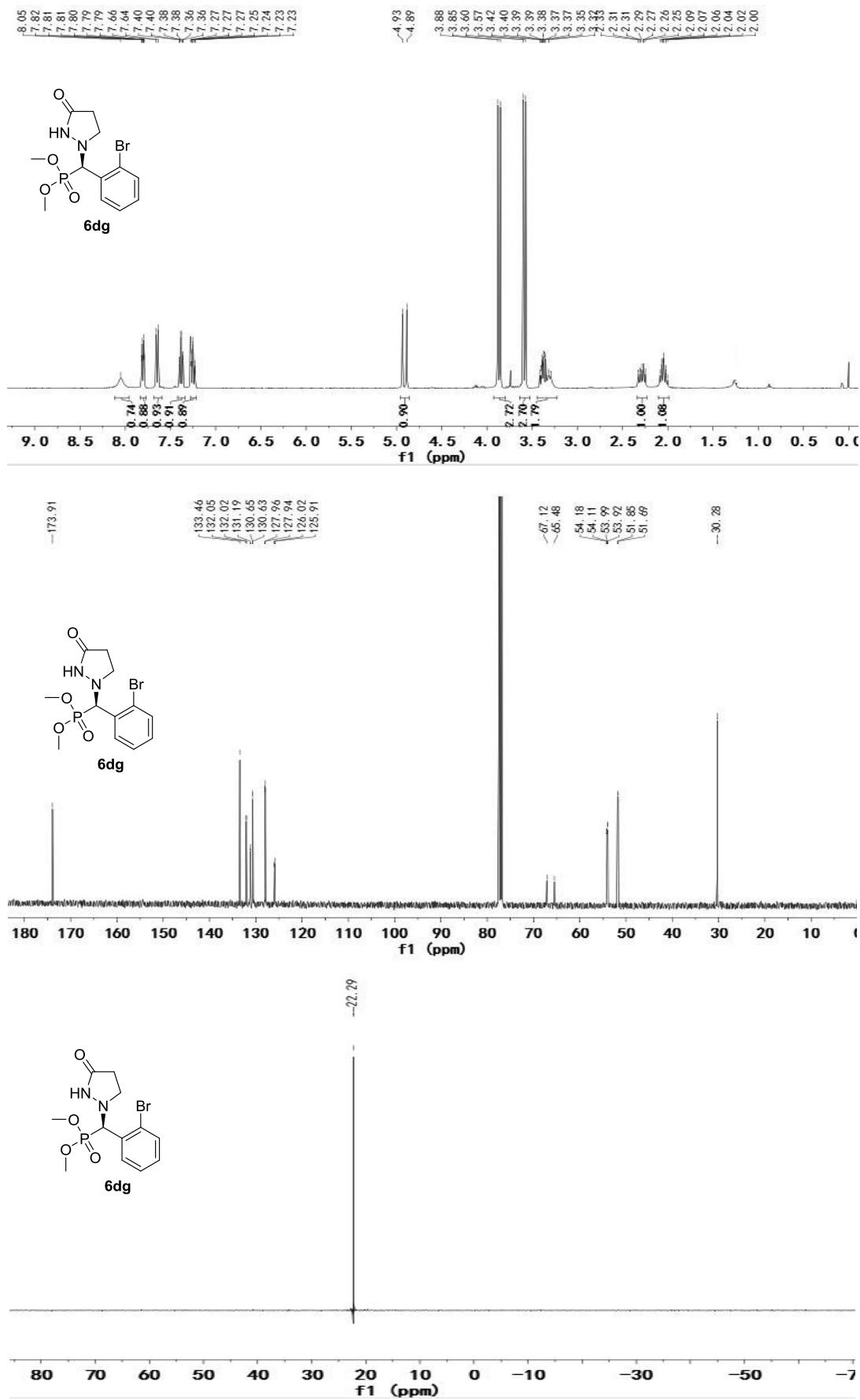
dimethyl (R)-((3-chlorophenyl)(3-oxopyrazolin-1-yl)methyl)phosphonate (6de)



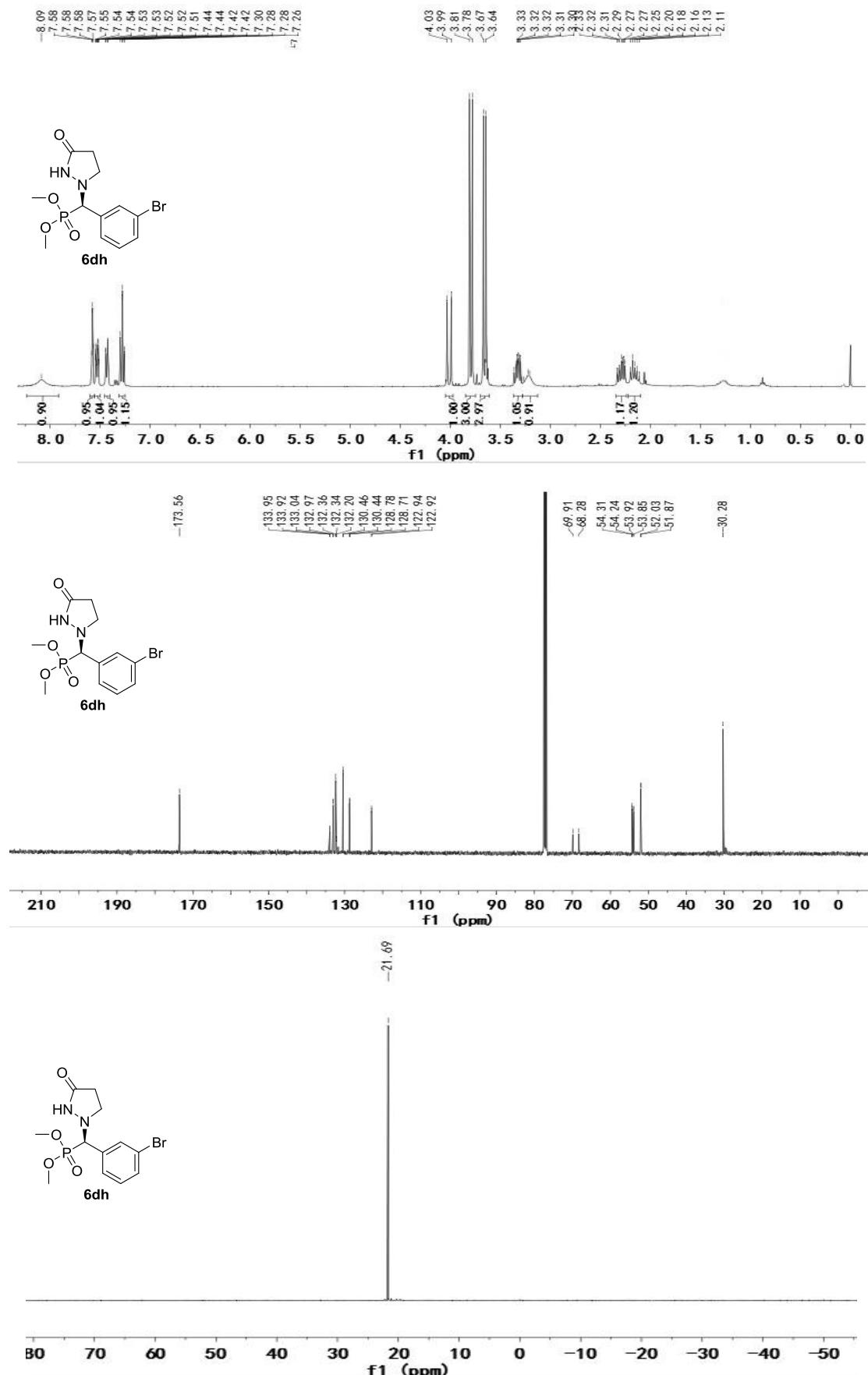
dimethyl (*R*)-((4-chlorophenyl)(3-oxopyrazolin-1-yl)methyl)phosphonate (6df)



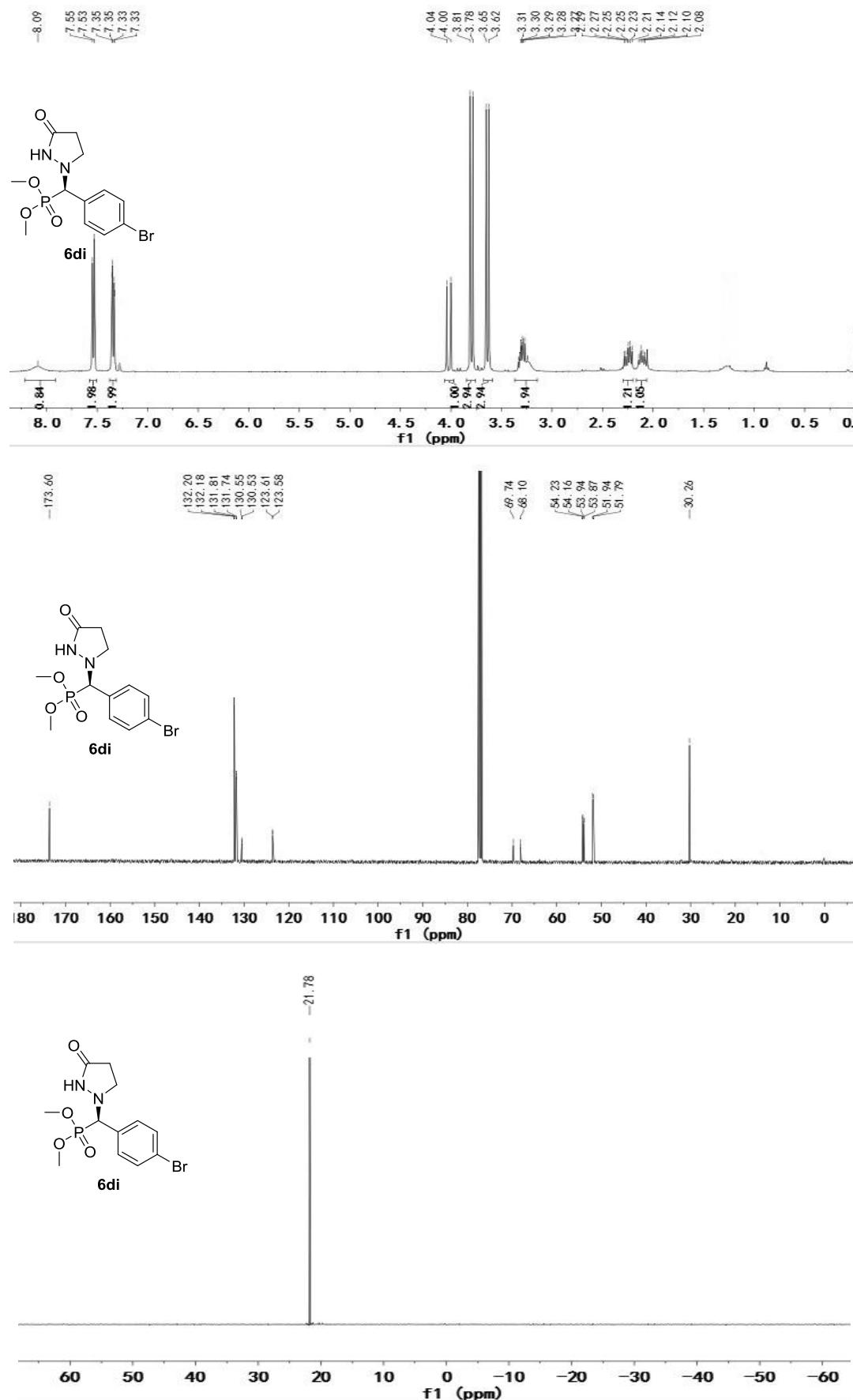
dimethyl (*R*)-((2-bromophenyl)(3-oxopyrazolin-1-yl)methyl)phosphonate (6dg)



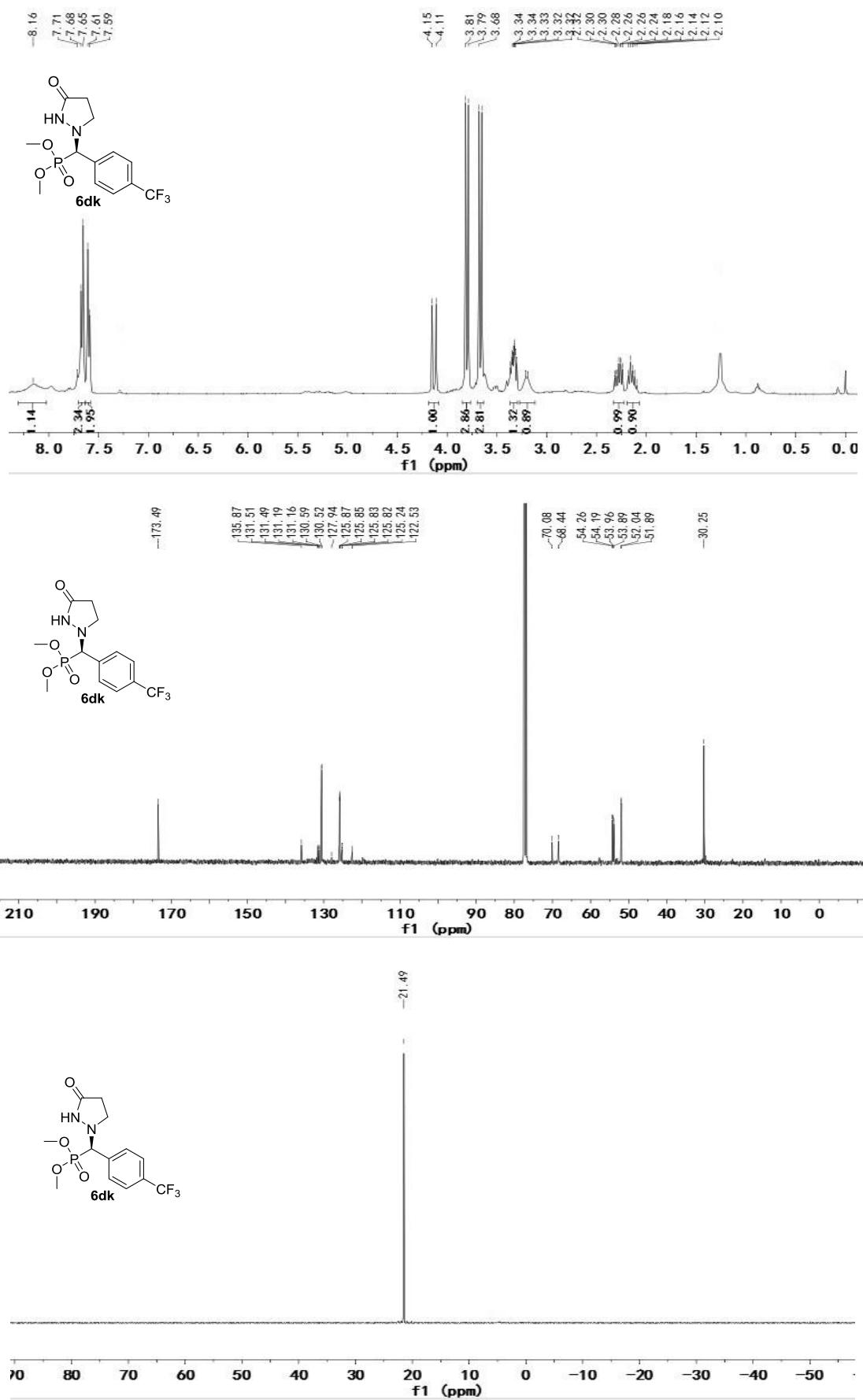
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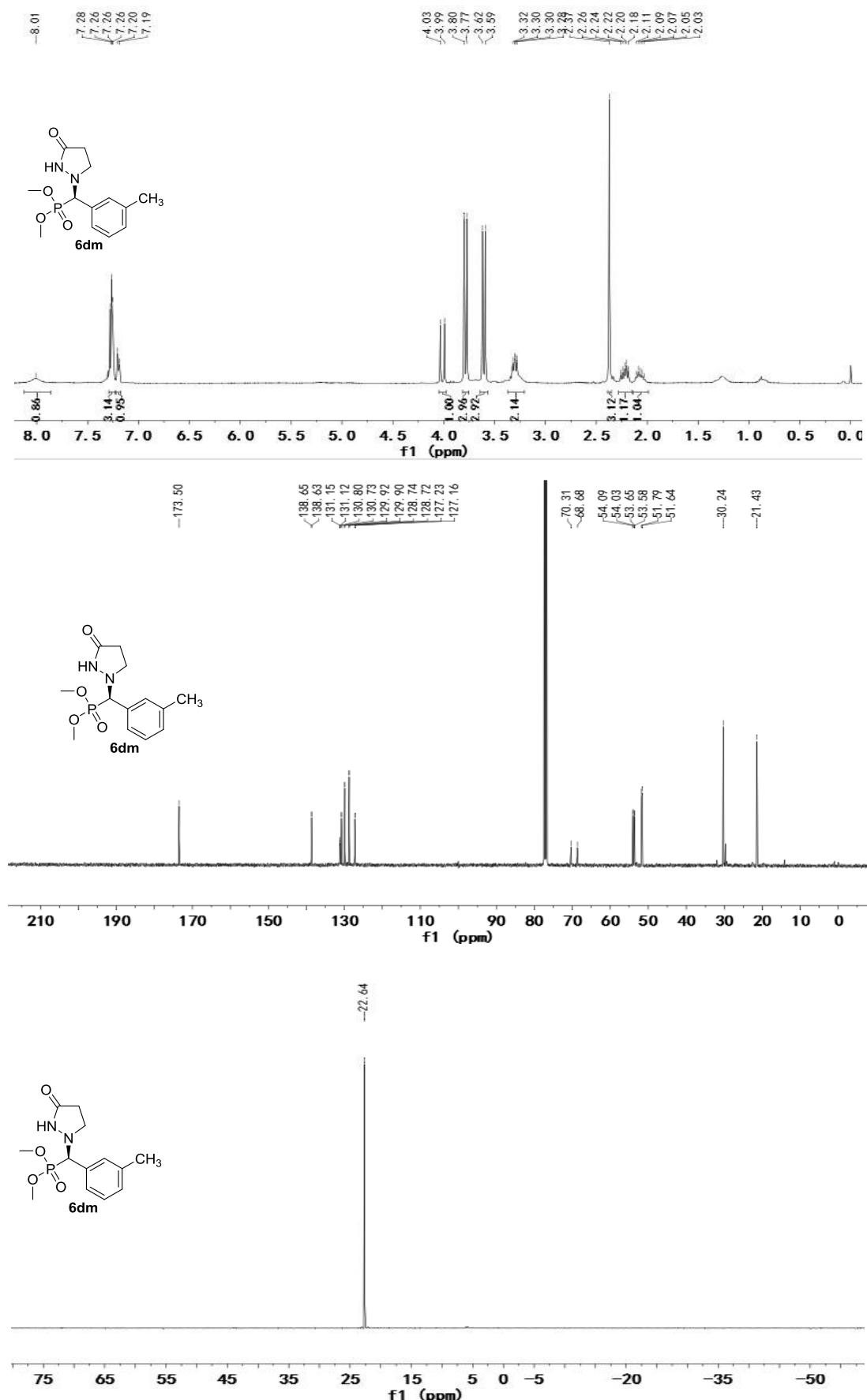
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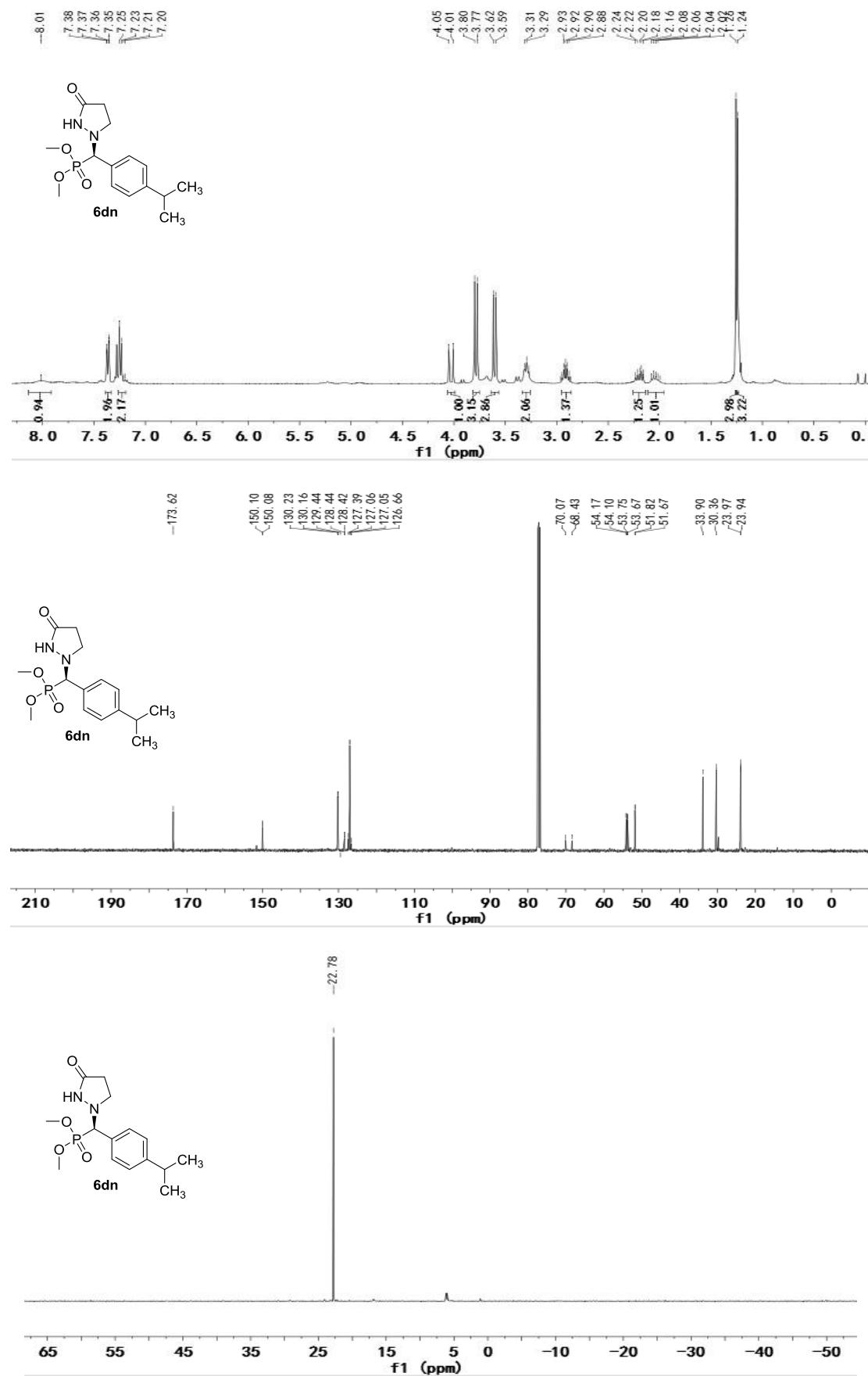
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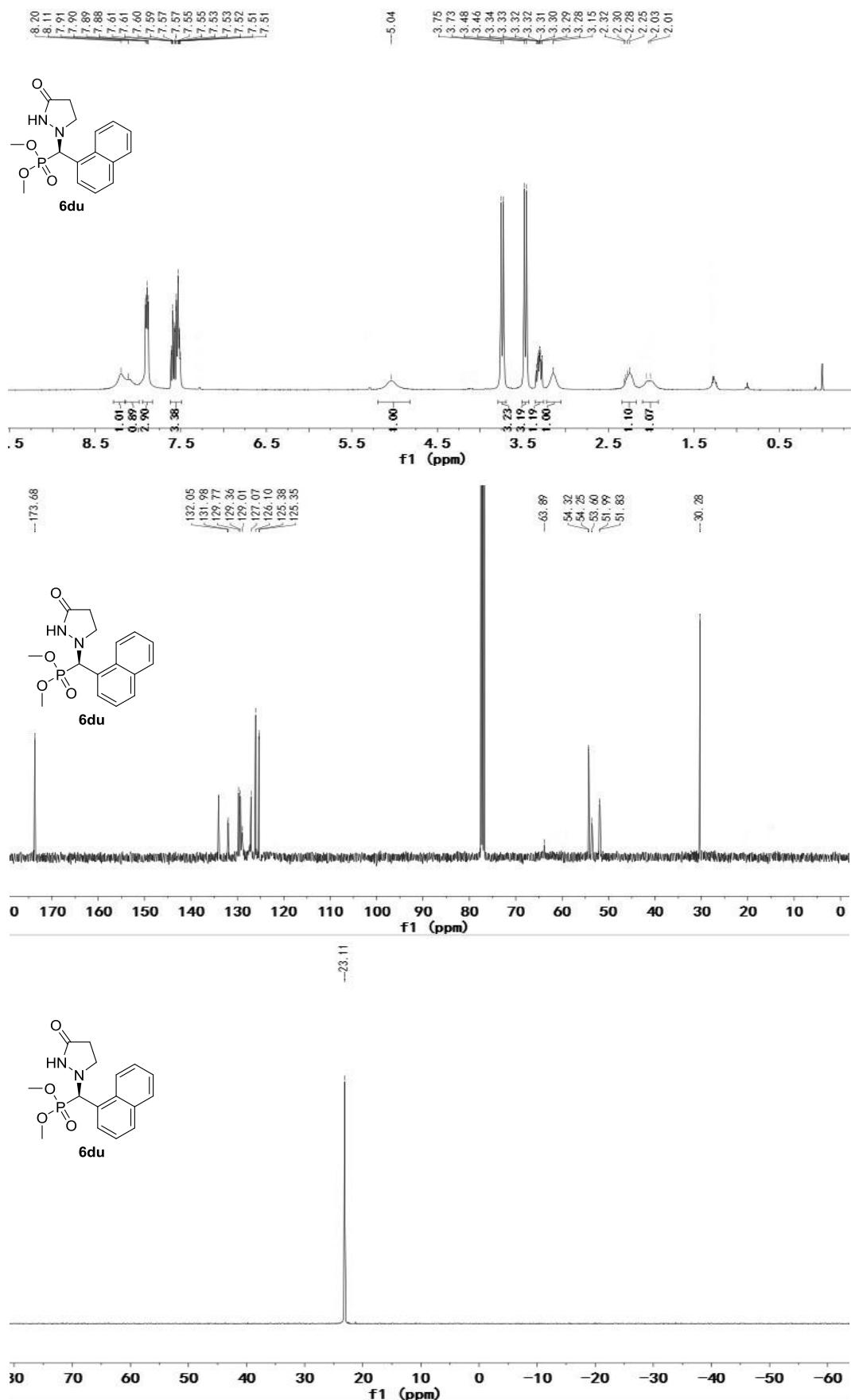
dimethyl (R)-((3-oxopyrazolidin-1-yl)(m-tolyl)methyl)phosphonate (6dm)



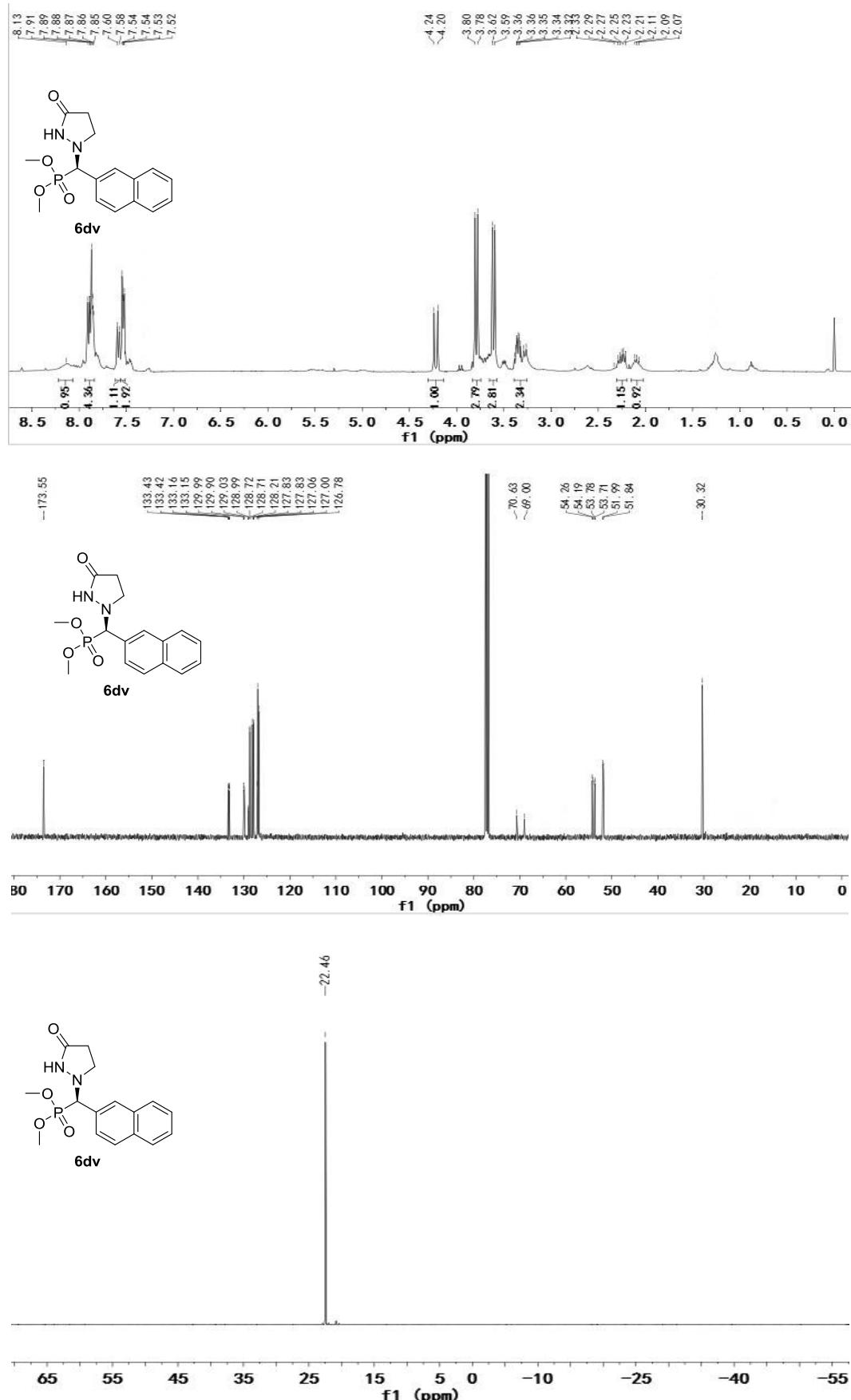
dimethyl (R)-((4-isopropylphenyl)(3-oxopyrazolidin-1-yl)methyl)phosphonate (6dn)



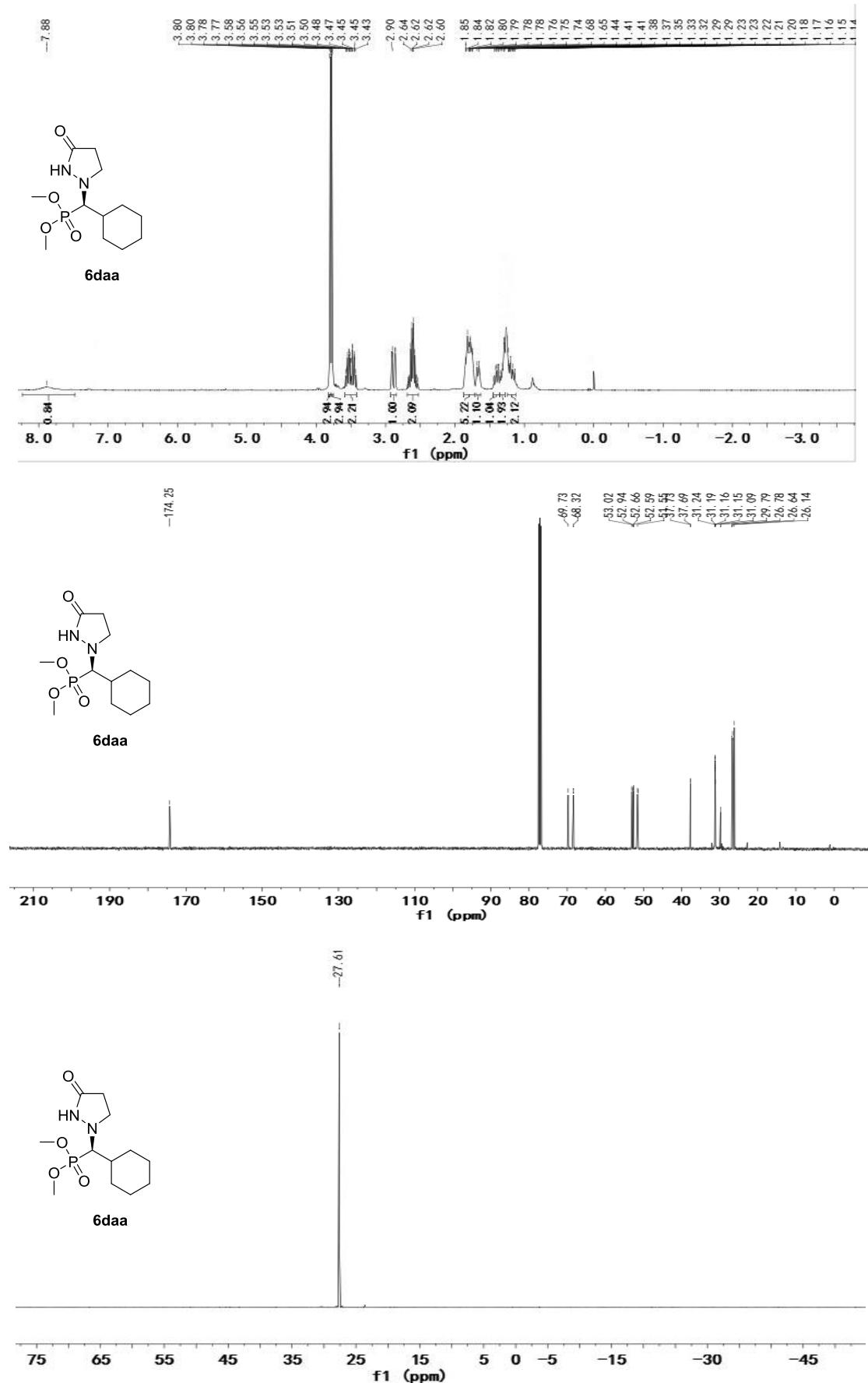
dimethyl (*R*)-(naphthalen-1-yl(3-oxopyrazolin-1-yl)methyl)phosphonate (6du)



dimethyl (R)-(naphthalen-2-yl(3-oxopyrazolin-1-yl)methyl)phosphonate (6dv)

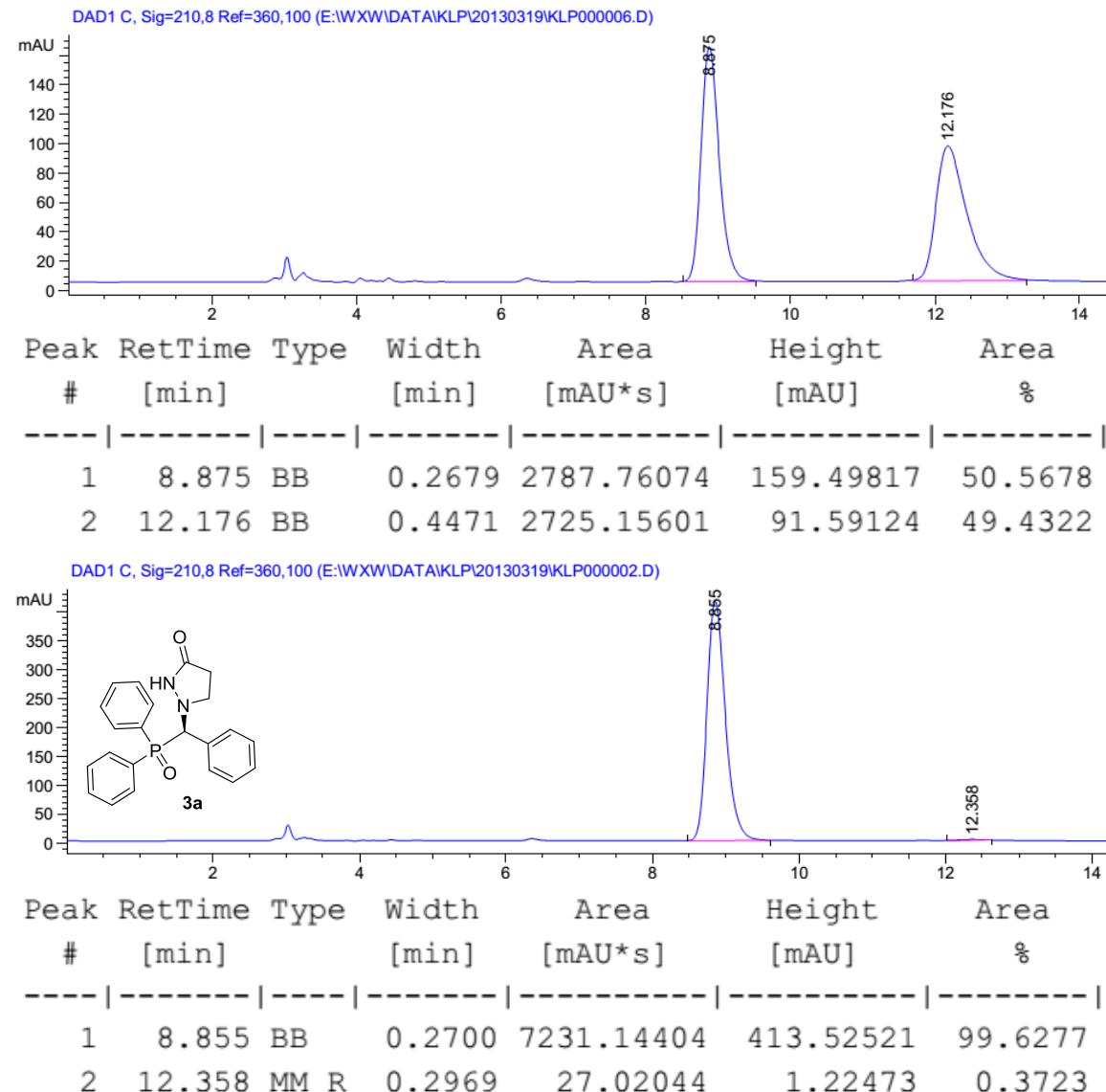


dimethyl (R)-(cyclohexyl(3-oxopyrazolidin-1-yl)methyl)phosphonate (6daa)

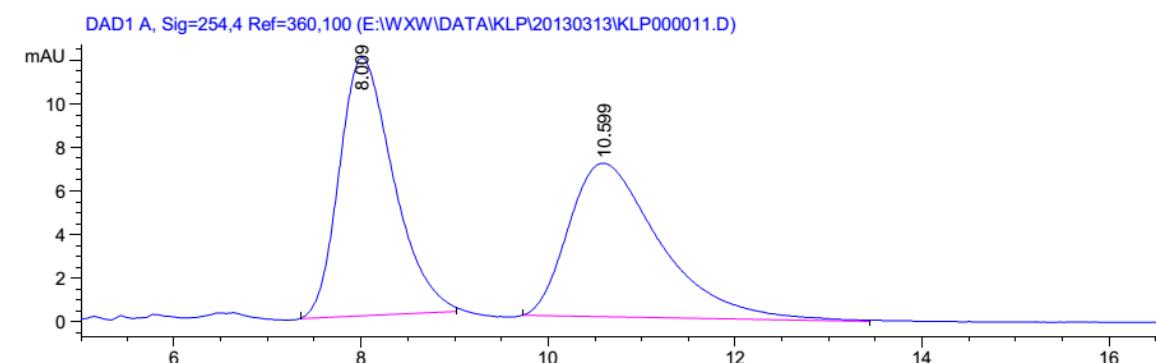


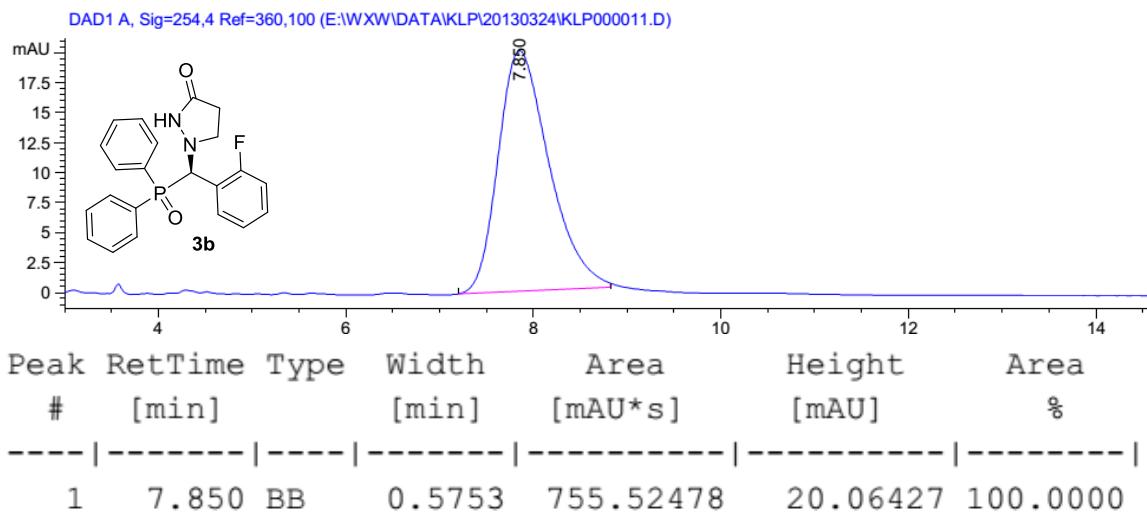
5. HPLC spectra

(R)-1-((diphenylphosphoryl)(phenyl)methyl)pyrazolidin-3-one (3a)

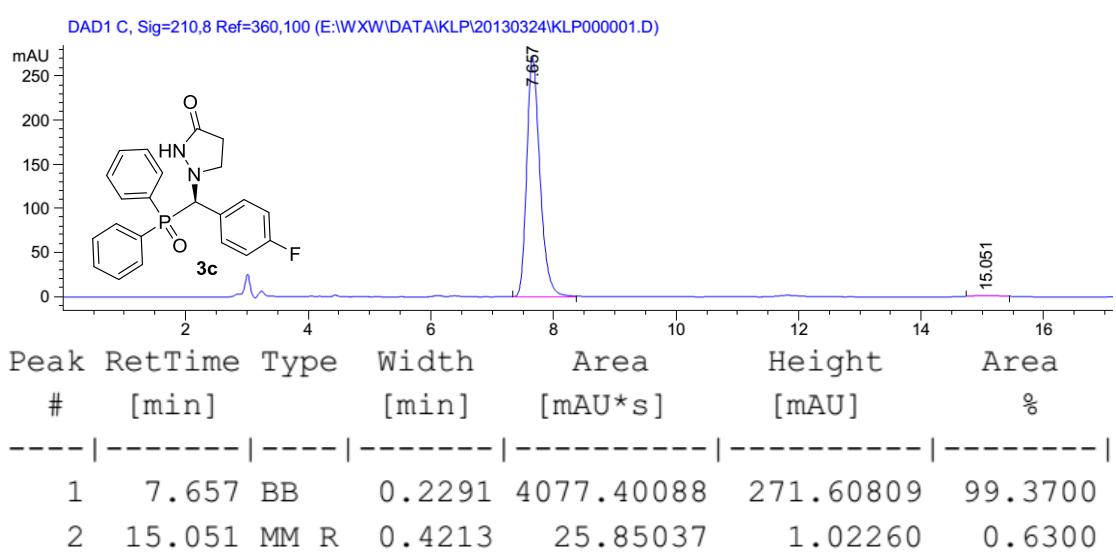
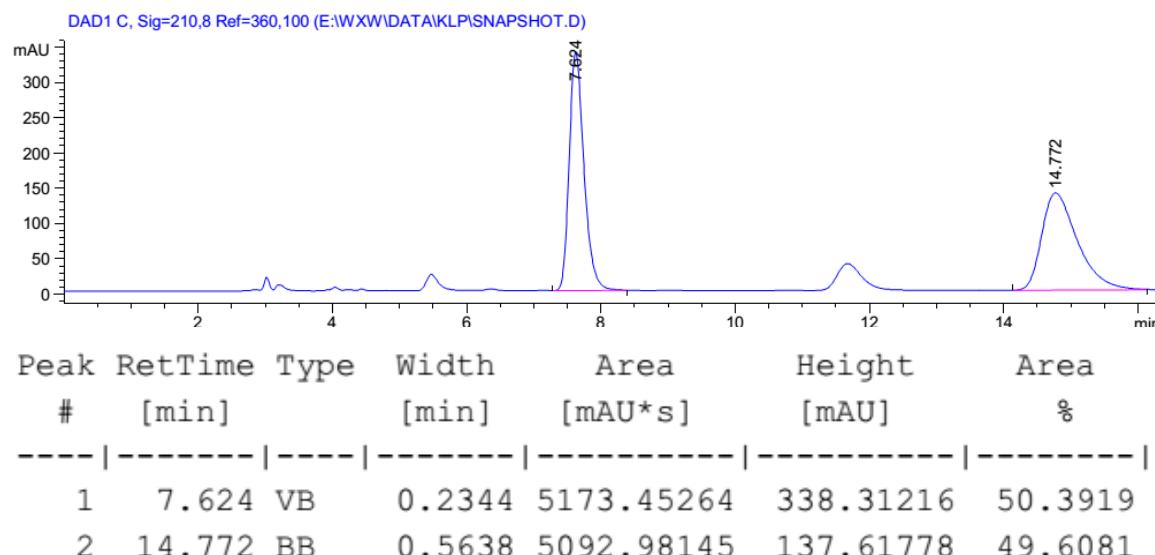


(R)-1-((diphenylphosphoryl)(2-fluorophenyl)methyl)pyrazolidin-3-one (3b)



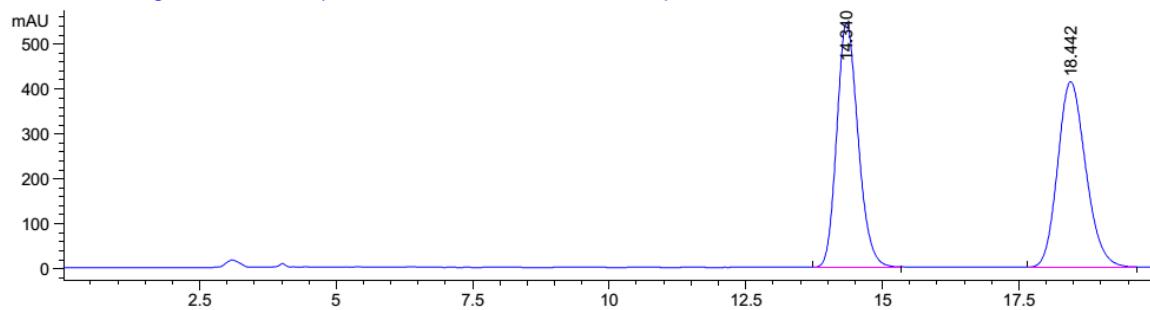


(R)-1-((diphenylphosphoryl)(4-fluorophenyl)methyl)pyrazolidin-3-one (3c)



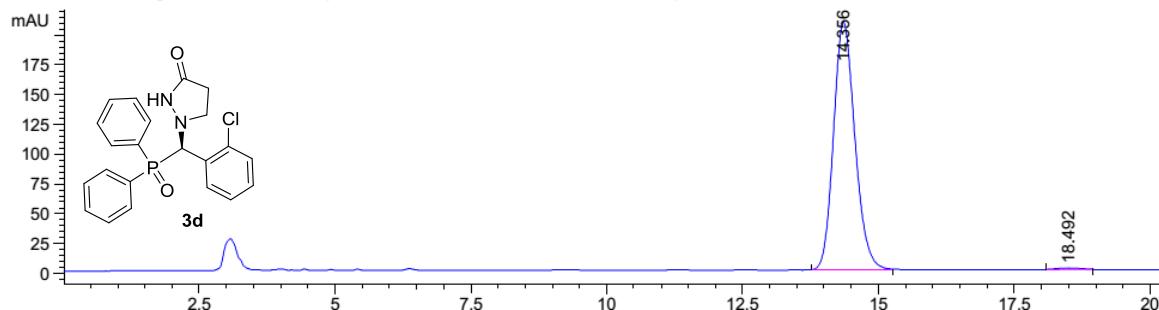
(R)-1-((2-chlorophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3d)

DAD1 C, Sig=210,8 Ref=360,100 (E:\WXW\DATA\KLP\20130330\KLP000003.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.340	BB	0.4208	1.47924e4	544.71106	49.9720
2	18.442	BB	0.5539	1.48090e4	413.47638	50.0280

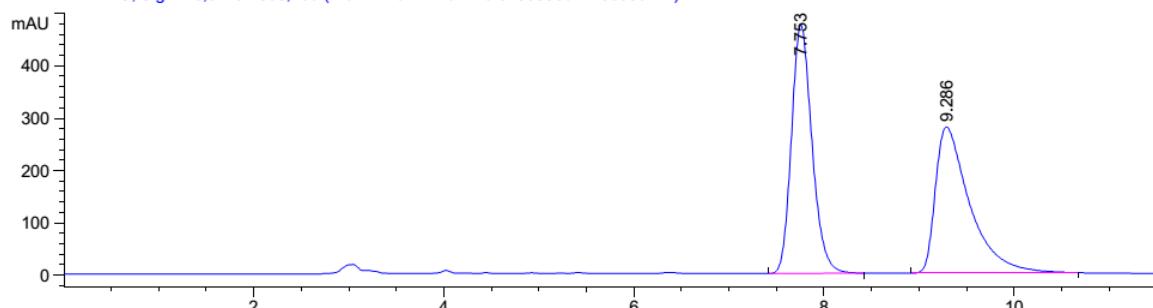
DAD1 C, Sig=210,8 Ref=360,100 (E:\WXW\DATA\KLP\20130404\KLP000001.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.356	BB	0.4233	5692.26367	207.97061	99.3375
2	18.492	MM R	0.4781	37.96147	1.32329	0.6625

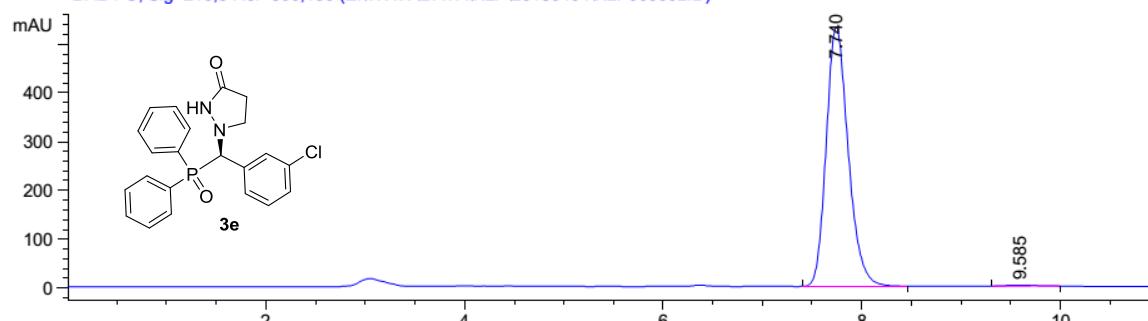
(R)-1-((3-chlorophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3e)

DAD1 C, Sig=210,8 Ref=360,100 (E:\WXW\DATA\KLP\20130330\KLP000002.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.753	BB	0.2317	7151.27588	474.97290	50.4252
2	9.286	BB	0.3716	7030.67432	279.39099	49.5748

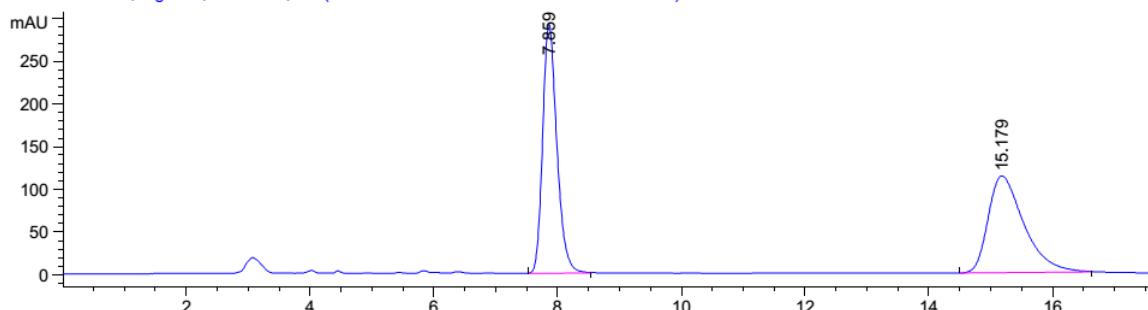
DAD1 C, Sig=210,8 Ref=360,100 (E:\WXW\DATA\KLP\20130404\KLP000002.D)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.740	BB	0.2376	8186.11182	531.66022	99.3447
2	9.585	MM R	0.4025	53.99435	2.23598	0.6553

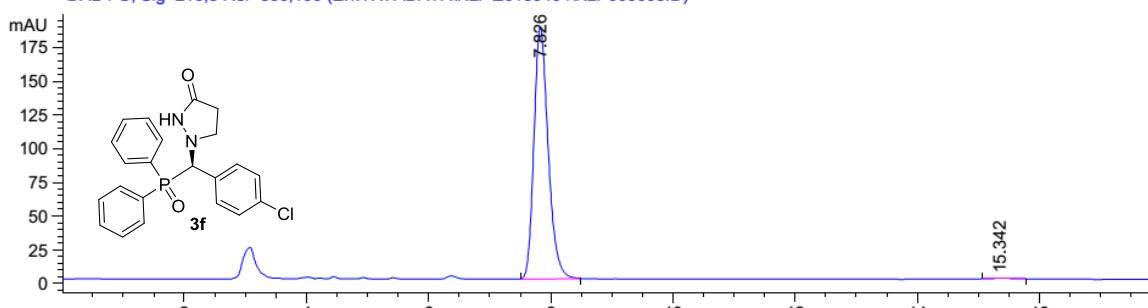
(R)-1-((4-chlorophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3f)

DAD1 C, Sig=210,8 Ref=360,100 (E:\WXW\DATA\KLP\20130330\KLP000001.D)



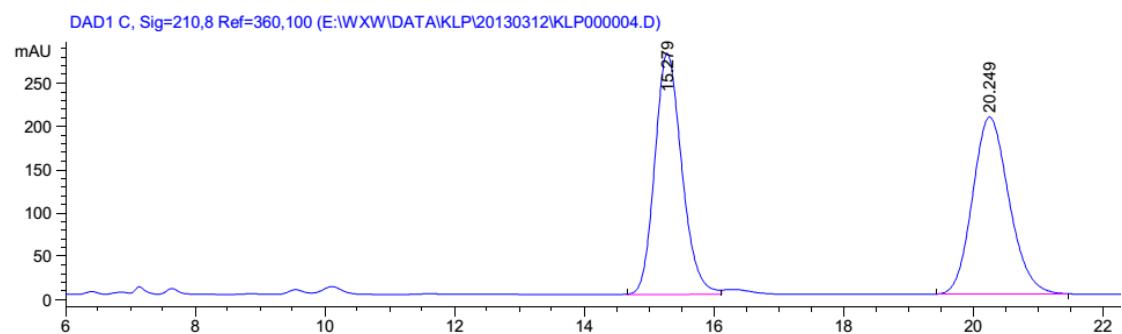
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.859	BB	0.2440	4637.36670	290.90717	50.4421
2	15.179	BB	0.6099	4556.08008	113.12265	49.5579

DAD1 C, Sig=210,8 Ref=360,100 (E:\WXW\DATA\KLP\20130404\KLP000003.D)

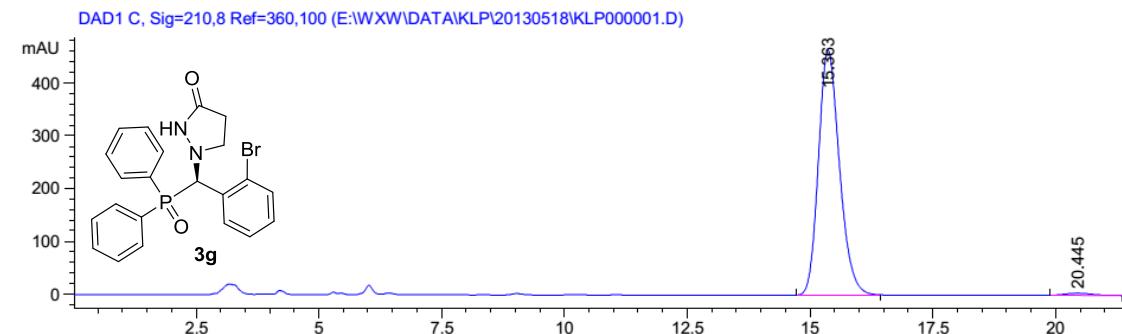


Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.826	BB	0.2490	3030.47485	187.09607	99.6504
2	15.342	MM R	0.4173	10.63286	4.24620e-1	0.3496

(R)-1-((2-bromophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3g)

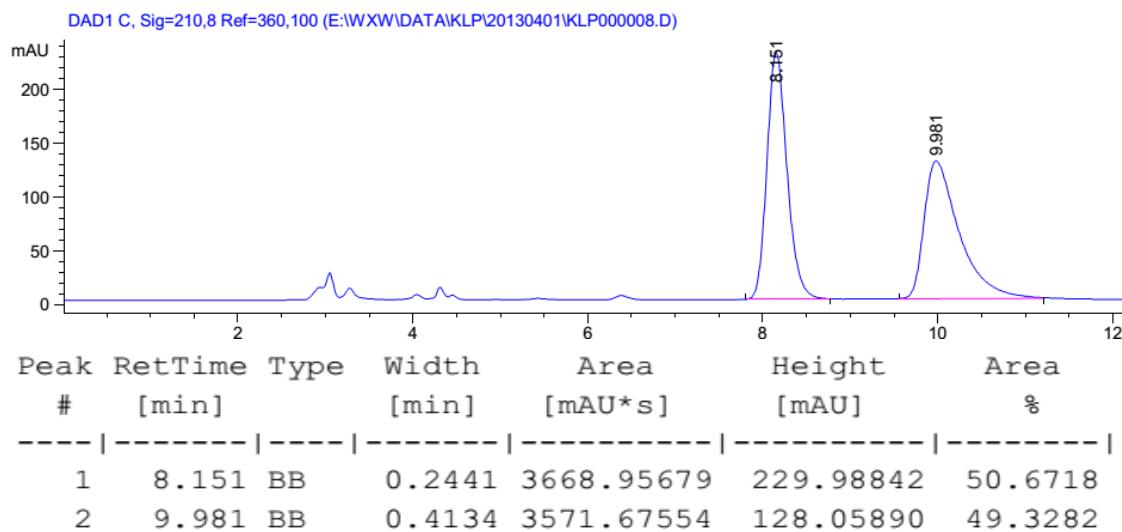


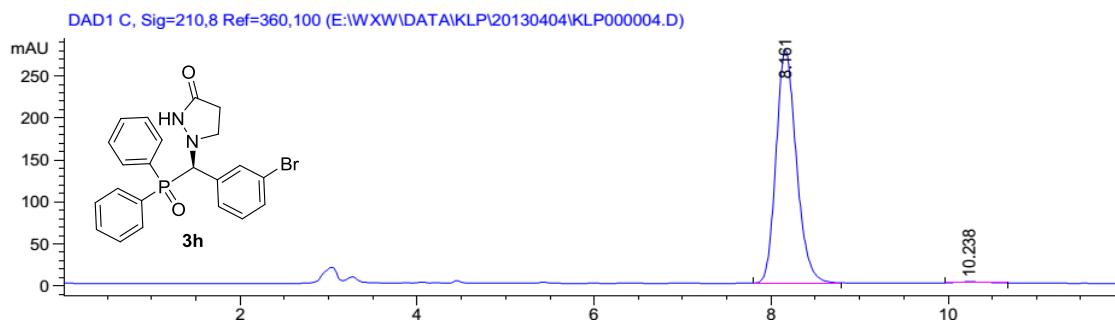
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.279	BB	0.4456	8061.16211	278.54541	50.1179
2	20.249	BB	0.6053	8023.22461	204.70392	49.8821



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.363	BB	0.4592	1.38324e4	464.84912	98.9142
2	20.445	BB	0.5527	151.84457	3.93032	1.0858

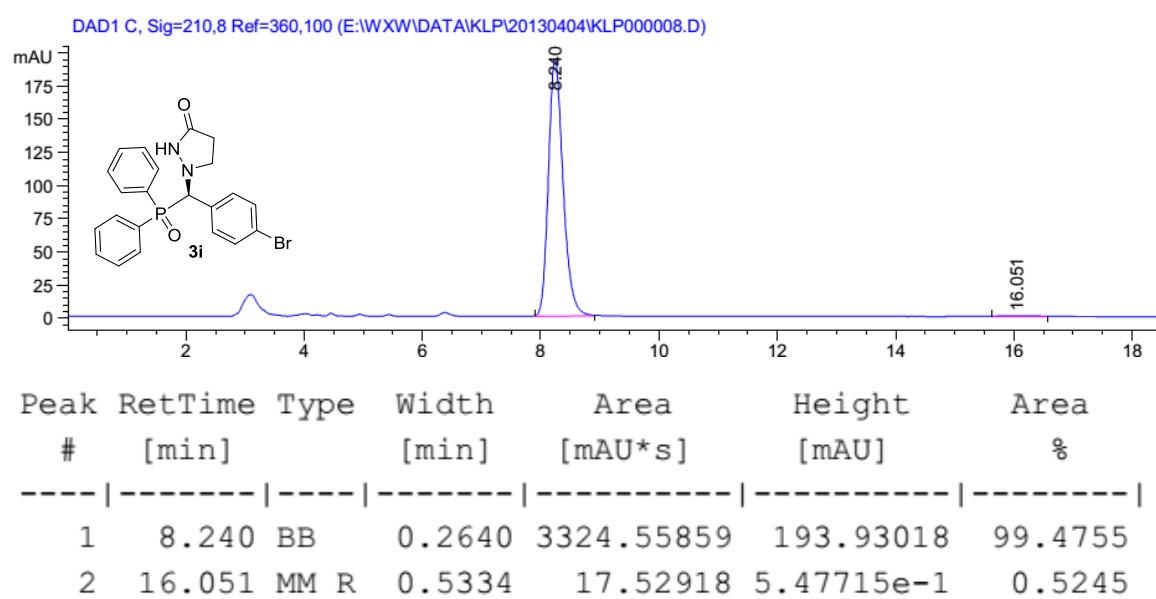
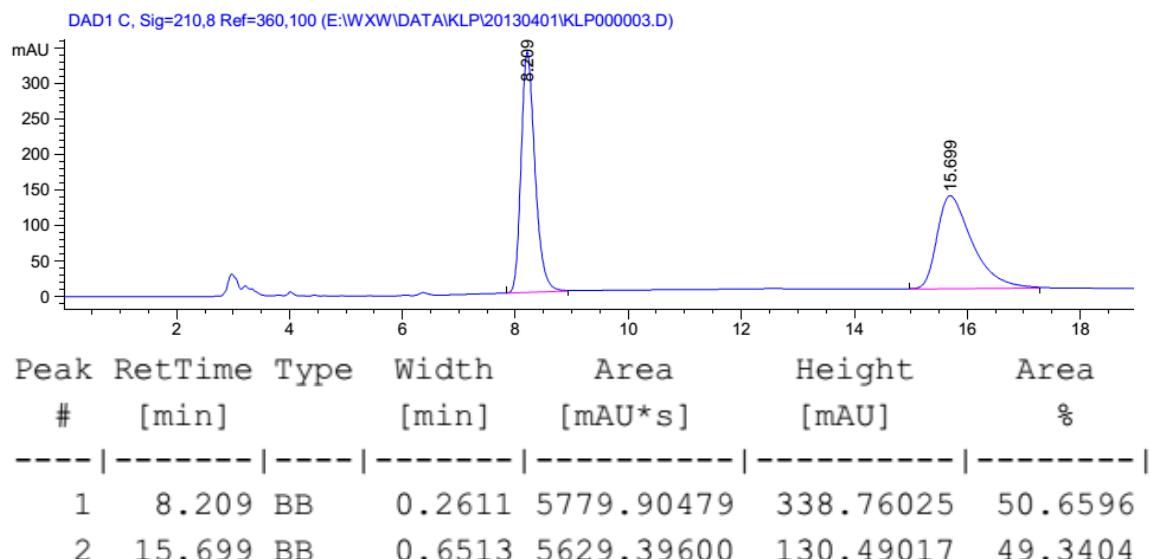
(R)-1-((3-bromophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3h)



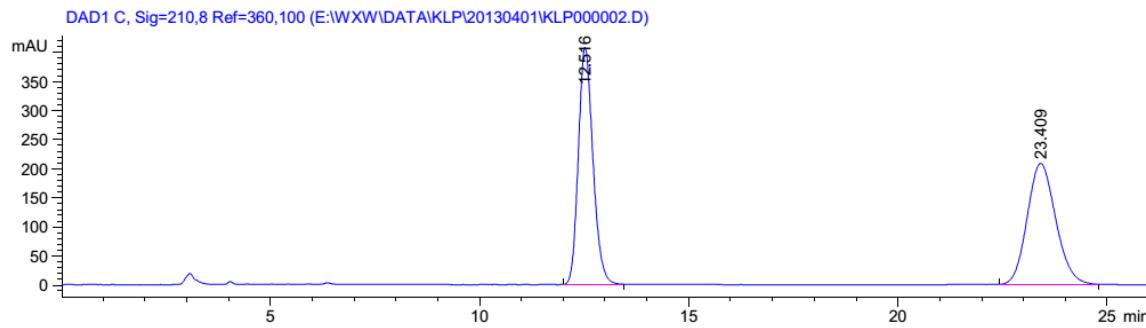


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.161	BB	0.2461	4436.00049	278.11060	99.3423
2	10.238	MM R	0.3981	29.36819	1.22965	0.6577

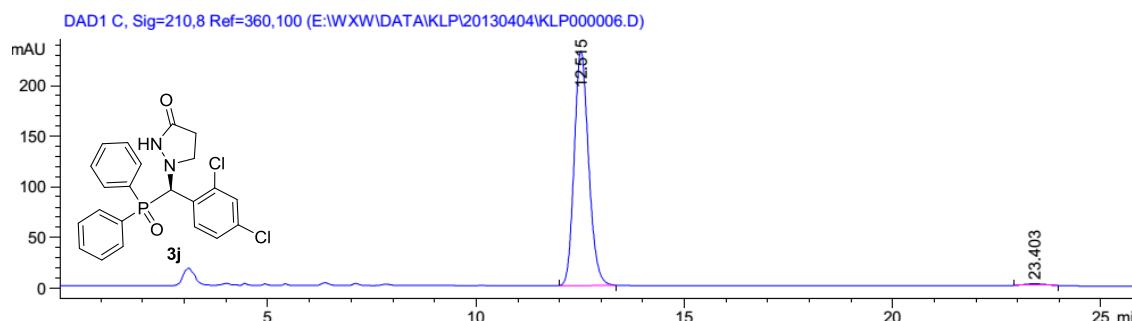
(R)-1-((4-bromophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3i)



(R)-1-((2,4-dichlorophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3j)

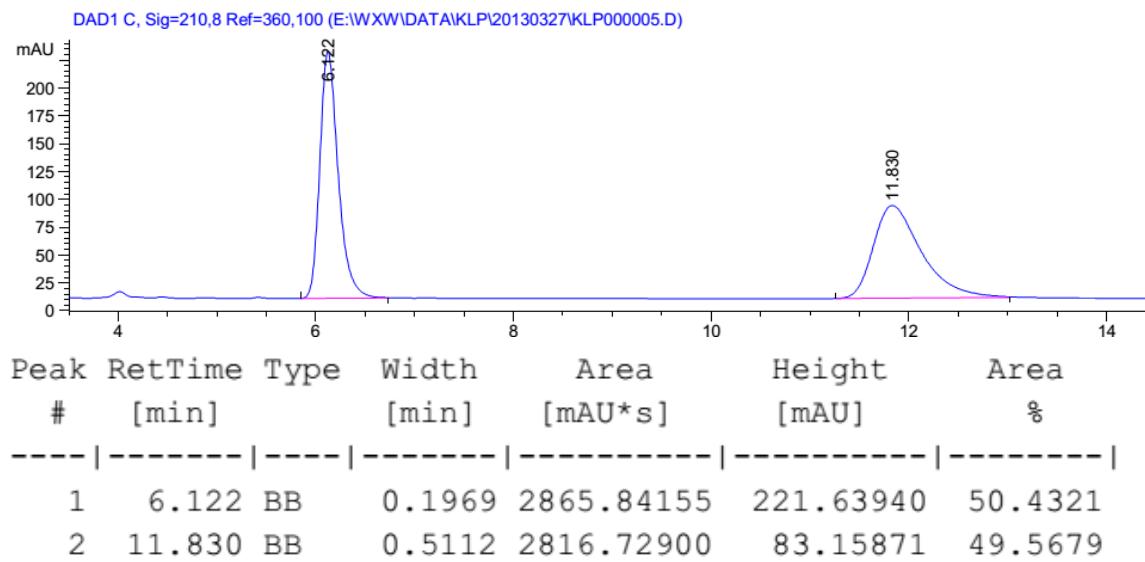


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.516	BB	0.3757	9898.37305	407.09955	49.9956
2	23.409	BB	0.7371	9900.13379	208.06346	50.0044



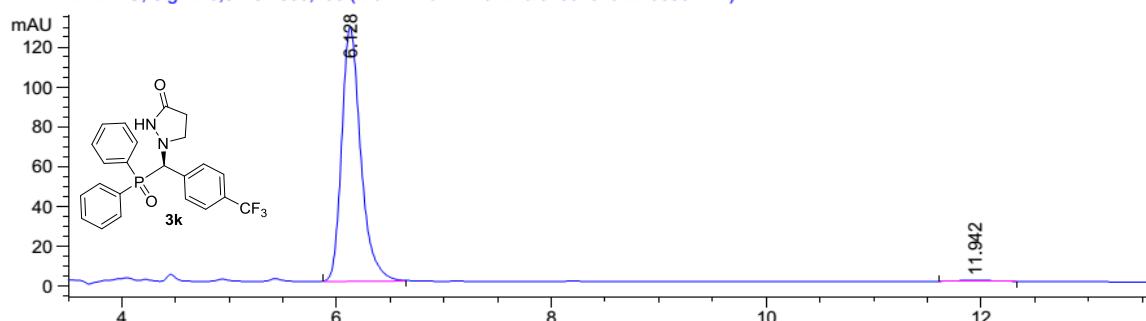
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.515	BB	0.3723	5576.27686	232.05925	98.9944
2	23.403	MM R	0.5957	56.64357	1.58468	1.0056

(R)-1-((diphenylphosphoryl)(4-(trifluoromethyl)phenyl)methyl)pyrazolidin-3-one (3k)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.122	BB	0.1969	2865.84155	221.63940	50.4321
2	11.830	BB	0.5112	2816.72900	83.15871	49.5679

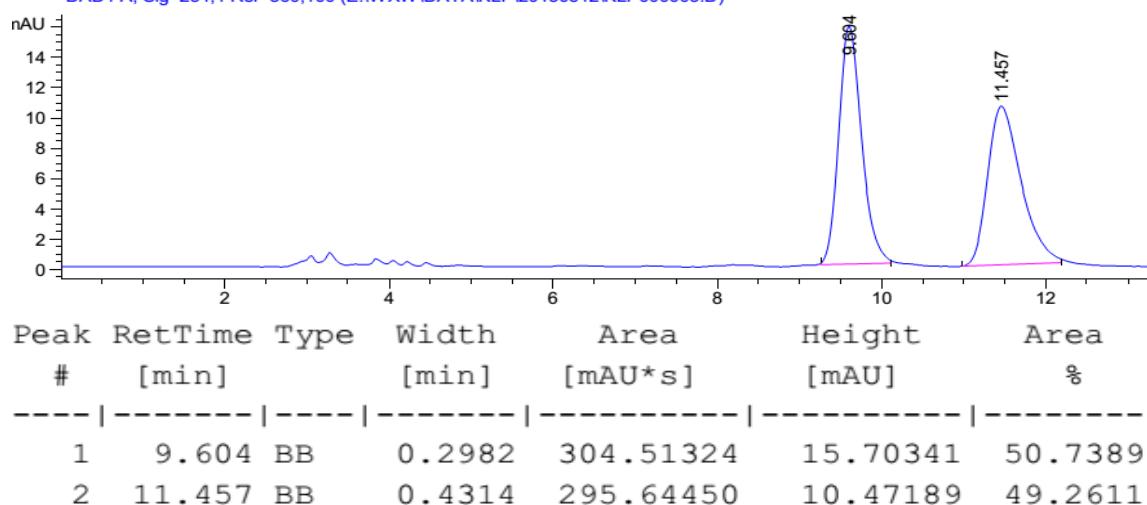
DAD1 C, Sig=210.8 Ref=360,100 (E:\WXW\DATA\KLP\20130404\KLP000011.D)



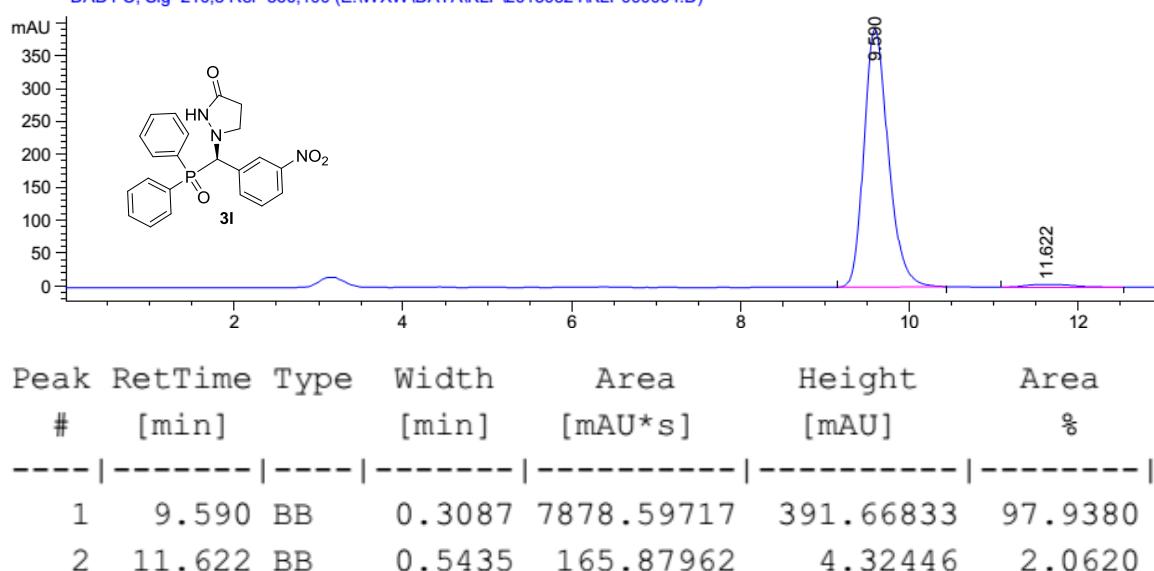
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.128	BB	0.1880	1575.10242	127.63464	99.3231
2	11.942	MM R	0.4067	10.73391	4.39832e-1	0.6769

(R)-1-((diphenylphosphoryl)(3-nitrophenyl)methyl)pyrazolidin-3-one (**3l**)

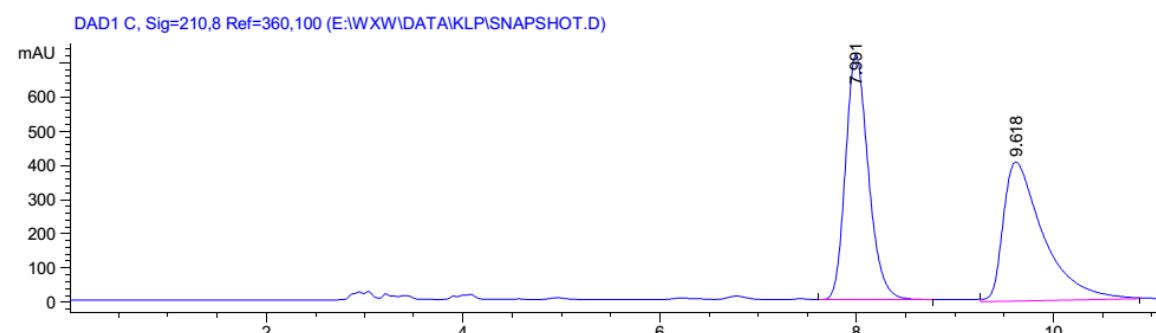
DAD1 A, Sig=254.4 Ref=360,100 (E:\WXW\DATA\KLP\20130312\KLP000003.D)



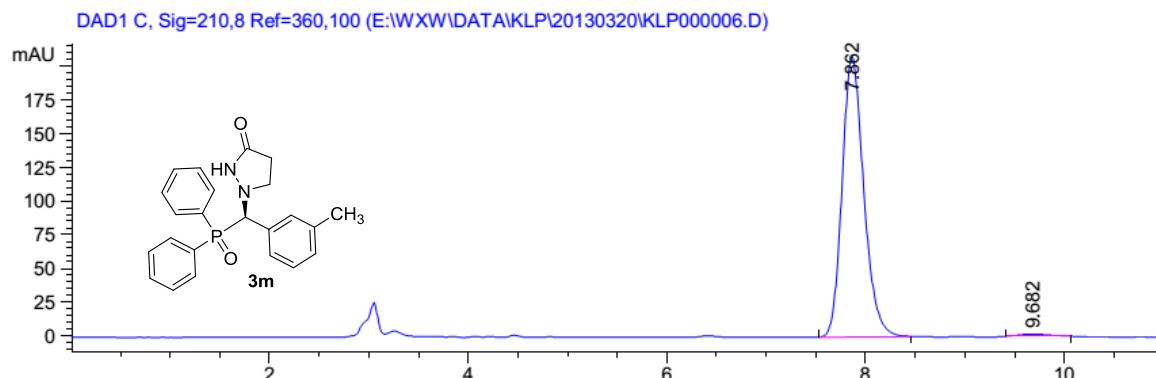
DAD1 C, Sig=210.8 Ref=360,100 (E:\WXW\DATA\KLP\20130324\KLP000004.D)



(R)-1-((diphenylphosphoryl)(m-tolyl)methyl)pyrazolidin-3-one (3m)

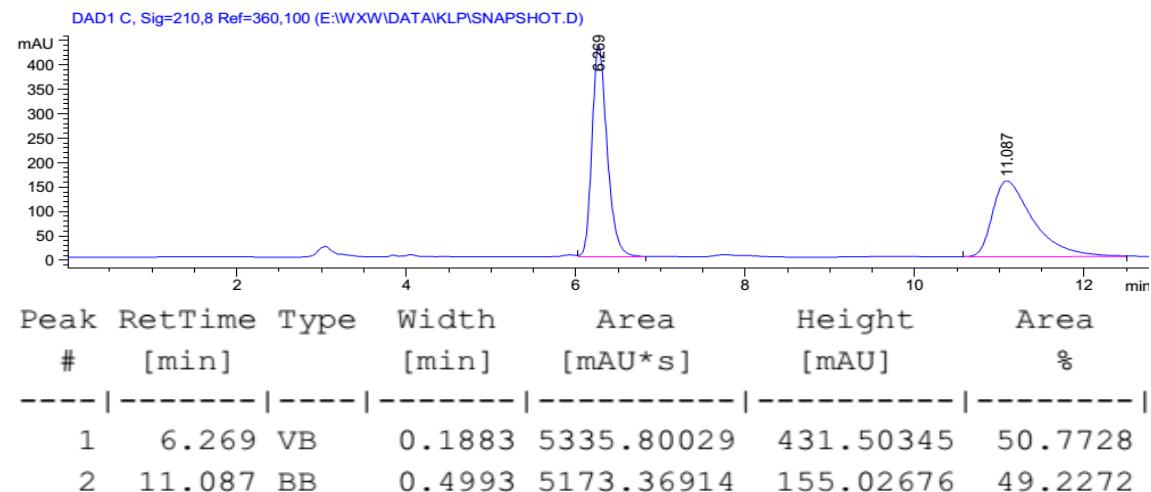


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.991	VB	0.2486	1.15708e4	715.72253	50.1785
2	9.618	MM R	0.4716	1.14885e4	405.96933	49.8215

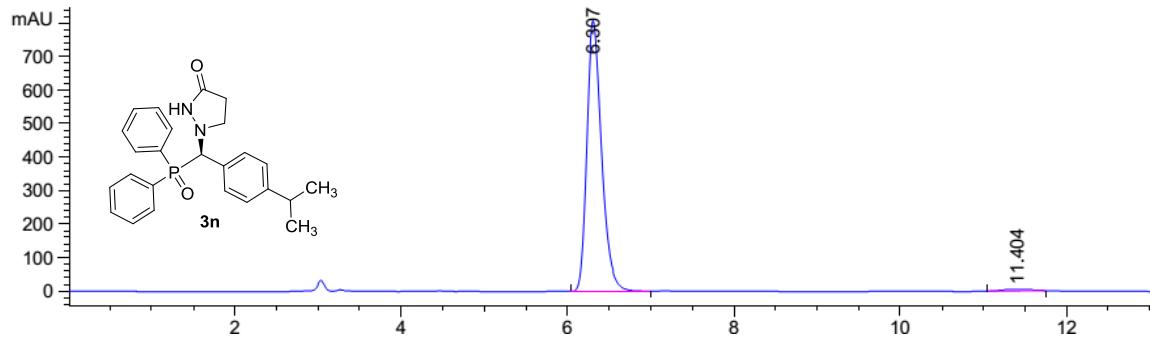


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.862	BB	0.2331	3154.88330	207.88969	98.9038
2	9.682	MM R	0.3602	34.96645	1.61810	1.0962

(R)-1-((diphenylphosphoryl)(4-isopropylphenyl)methyl)pyrazolidin-3-one (3n)

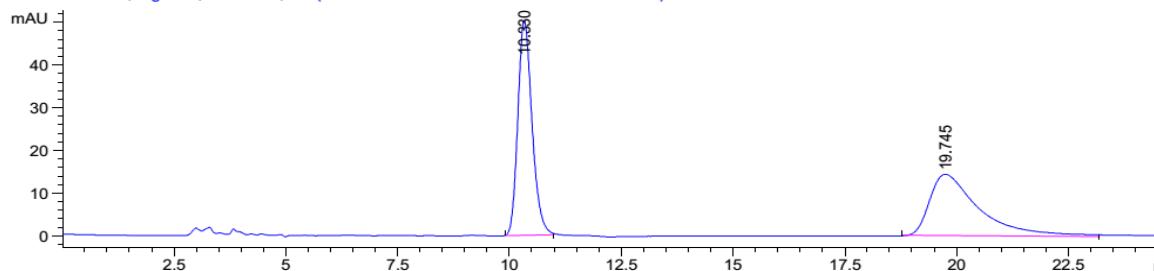


DAD1 C, Sig=210,8 Ref=360,100 (E:\WXW\DATA\KLP\20130320\KLP000002.D)

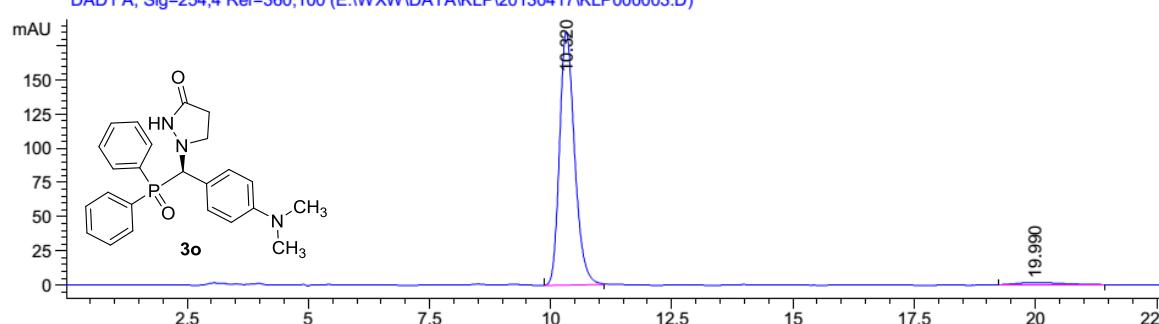


(R)-1-((4-(dimethylamino)phenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3o)

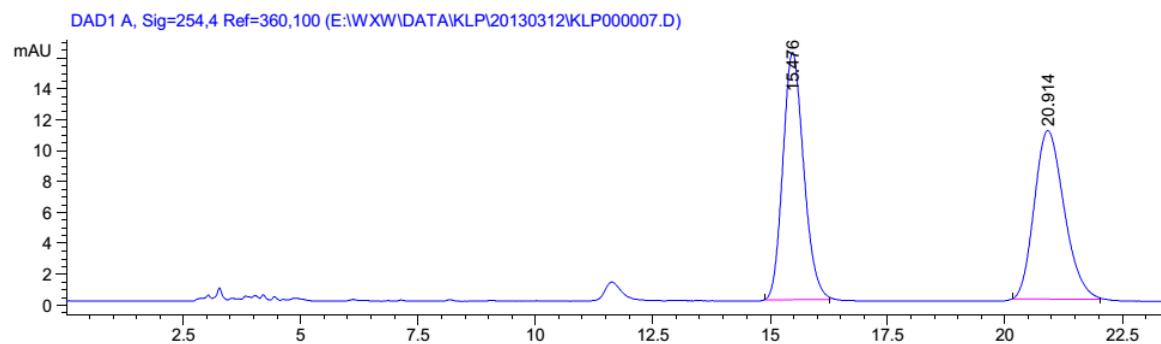
DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\KLP\20130401\KLP000005.D)



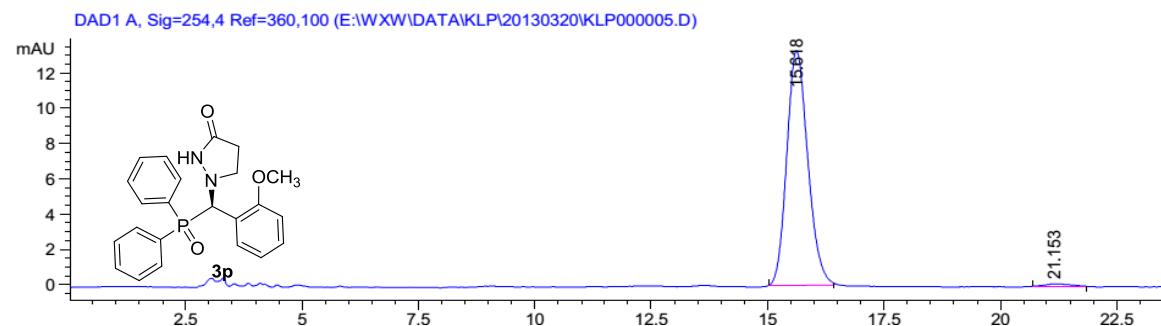
DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\KLP\20130417\KLP000003.D)



(R)-1-((diphenylphosphoryl)(2-methoxyphenyl)methyl)pyrazolidin-3-one (3p)

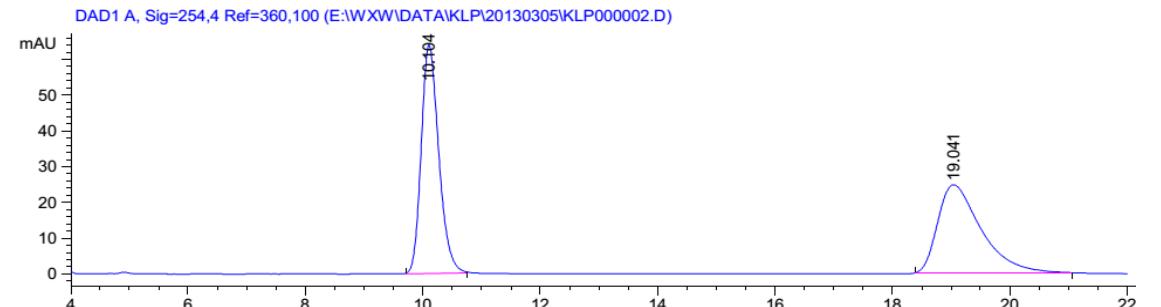


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.476	BB	0.4763	493.92920	15.99509	50.6318
2	20.914	BB	0.6722	481.60318	10.88529	49.3682



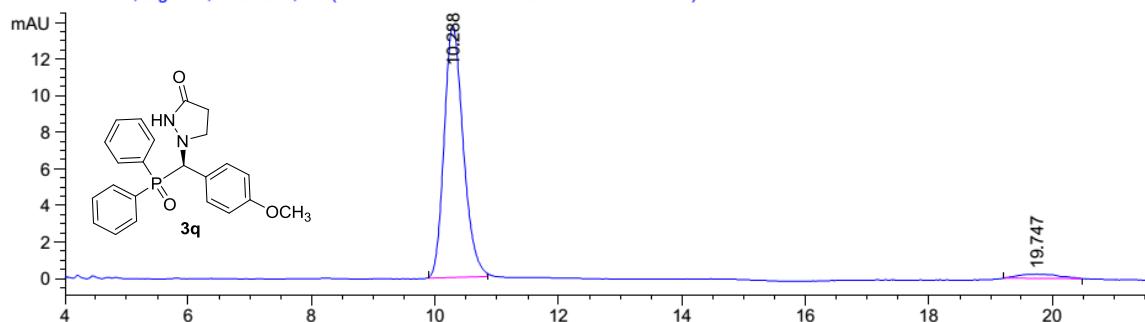
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.618	BB	0.4839	417.53815	13.31472	98.7755
2	21.153	MM R	0.6351	5.17620	1.35841e-1	1.2245

(R)-1-((diphenylphosphoryl)(4-methoxyphenyl)methyl)pyrazolidin-3-one (3q)



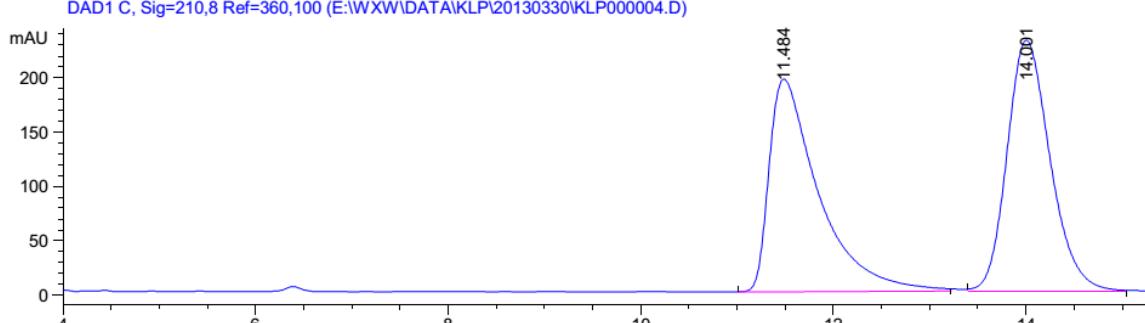
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.104	BB	0.3184	1328.99146	63.97220	50.8025
2	19.041	MM R	0.8641	1287.00281	24.82384	49.1975

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\KLP\20130320\KLP000007.D)

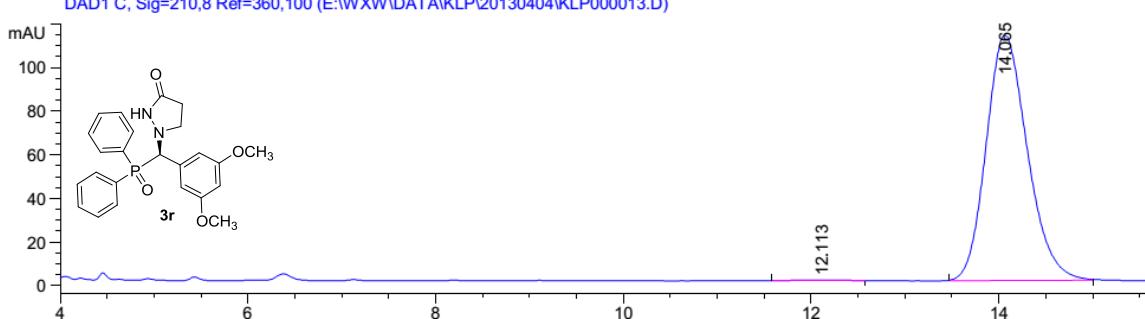


(R)-1-((3,5-dimethoxyphenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (**3r**)

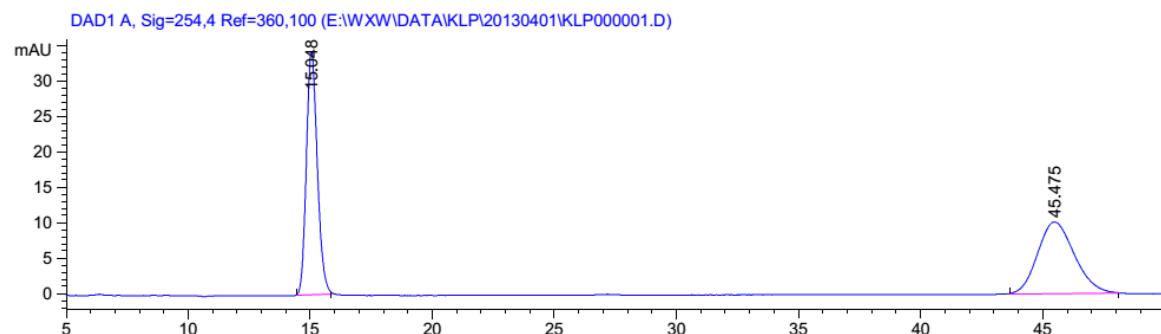
DAD1 C, Sig=210,8 Ref=360,100 (E:\WXW\DATA\KLP\20130330\KLP000004.D)



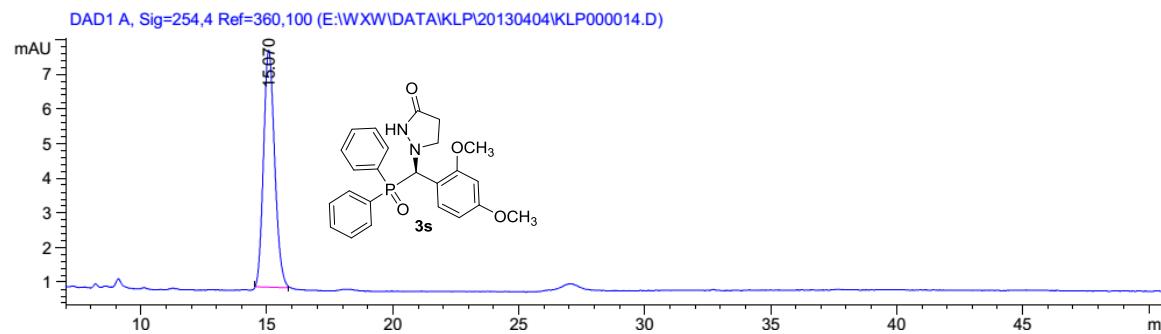
DAD1 C, Sig=210,8 Ref=360,100 (E:\WXW\DATA\KLP\20130404\KLP000013.D)



(R)-1-((2, 4-dimethoxyphenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3s)

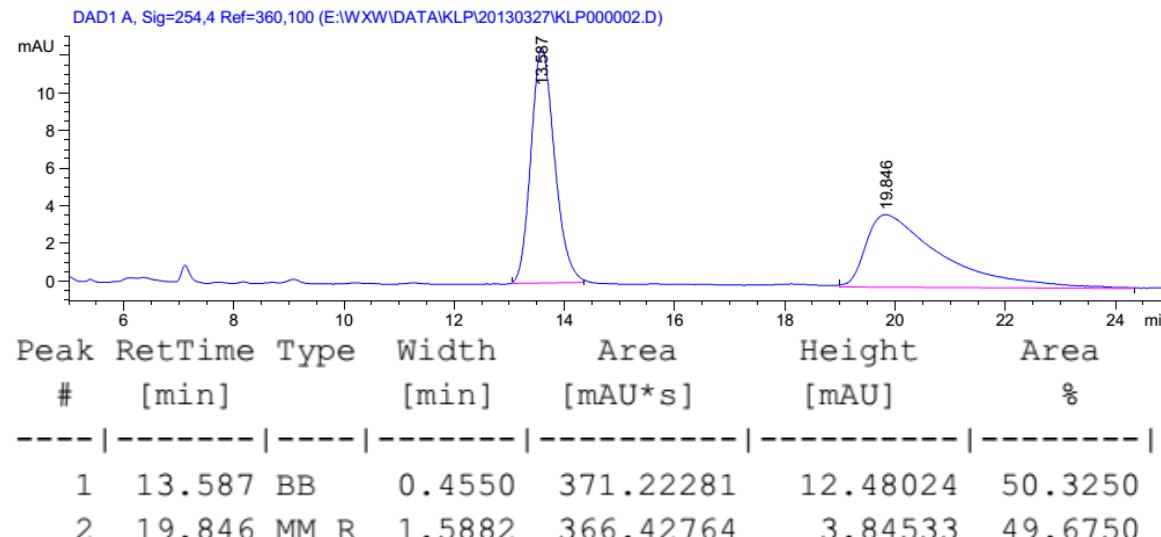


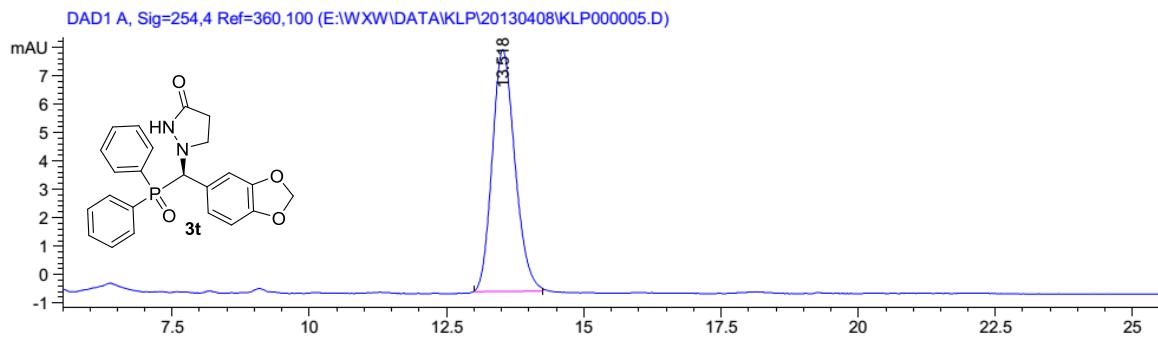
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.048	BB	0.4815	1067.99023	34.27734	50.2072
2	45.475	MM R	1.7479	1059.17639	10.09956	49.7928



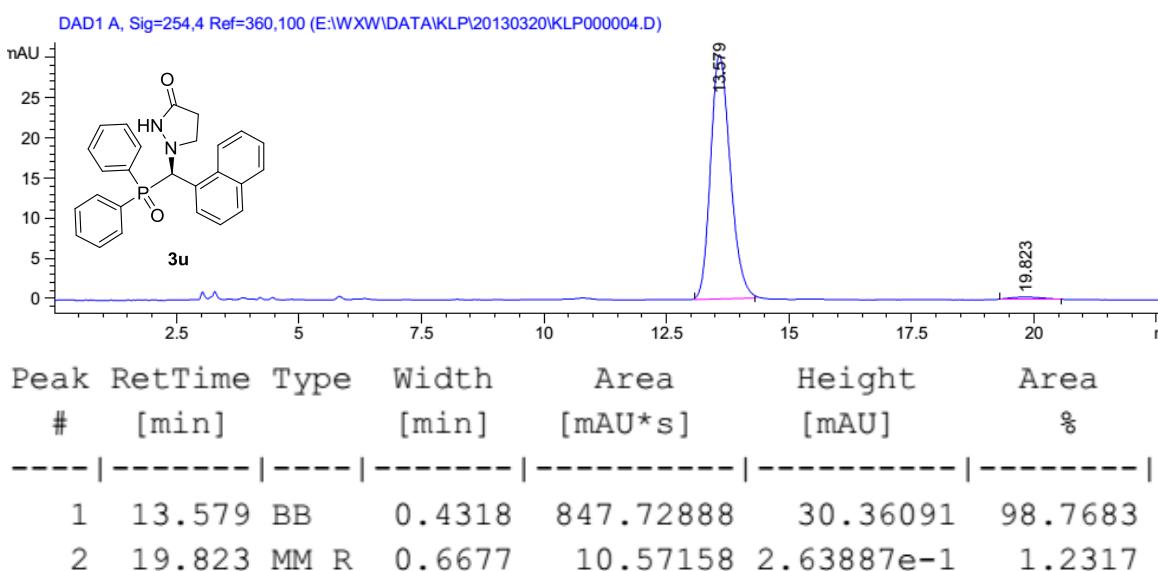
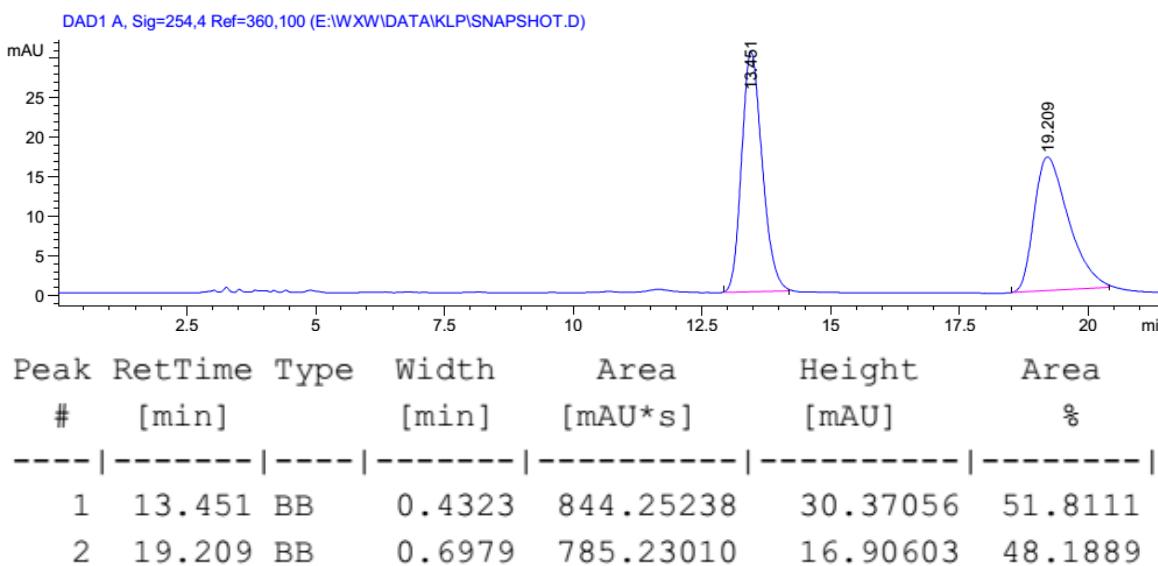
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.070	BB	0.4633	209.68013	6.84697	100.0000

(R)-1-(benzo[d][1,3]dioxol-5-yl(diphenylphosphoryl)methyl)pyrazolidin-3-one (3t)

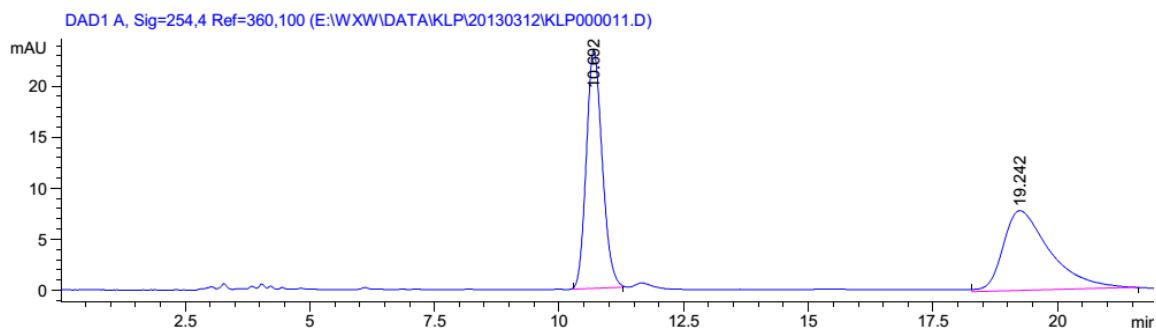




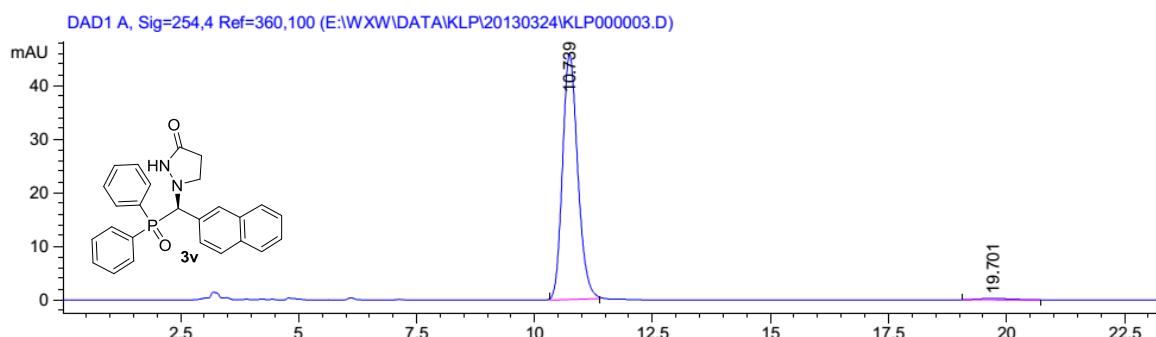
(R)-1-((diphenylphosphoryl)(naphthalen-1-yl)methyl)pyrazolidin-3-one (3u)



(R)-1-((diphenylphosphoryl)(naphthalen-2-yl)methyl)pyrazolidin-3-one (3v)

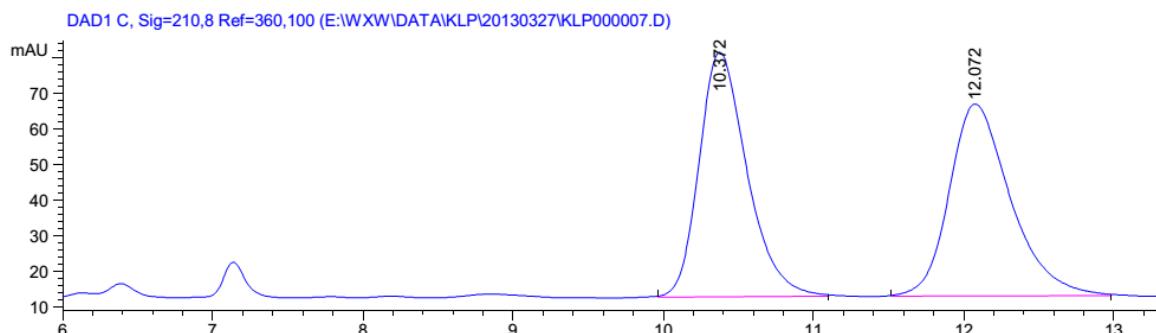


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.692	BB	0.3434	519.26312	23.35177	50.3802
2	19.242	MM R	1.0874	511.42581	7.83842	49.6198

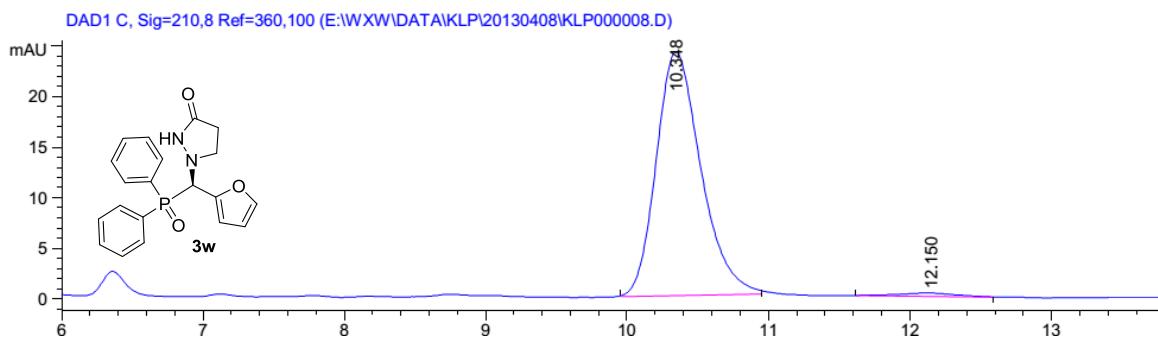


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.739	BB	0.3433	1026.42529	45.83599	98.8049
2	19.701	MM R	0.8908	12.41479	2.32271e-1	1.1951

(R)-1-((diphenylphosphoryl)(furan-3-yl)methyl)pyrazolidin-3-one (3w)

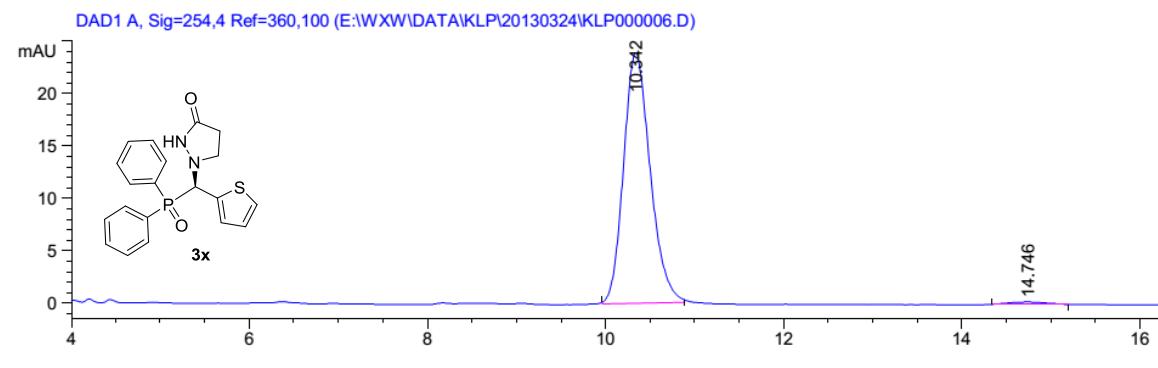
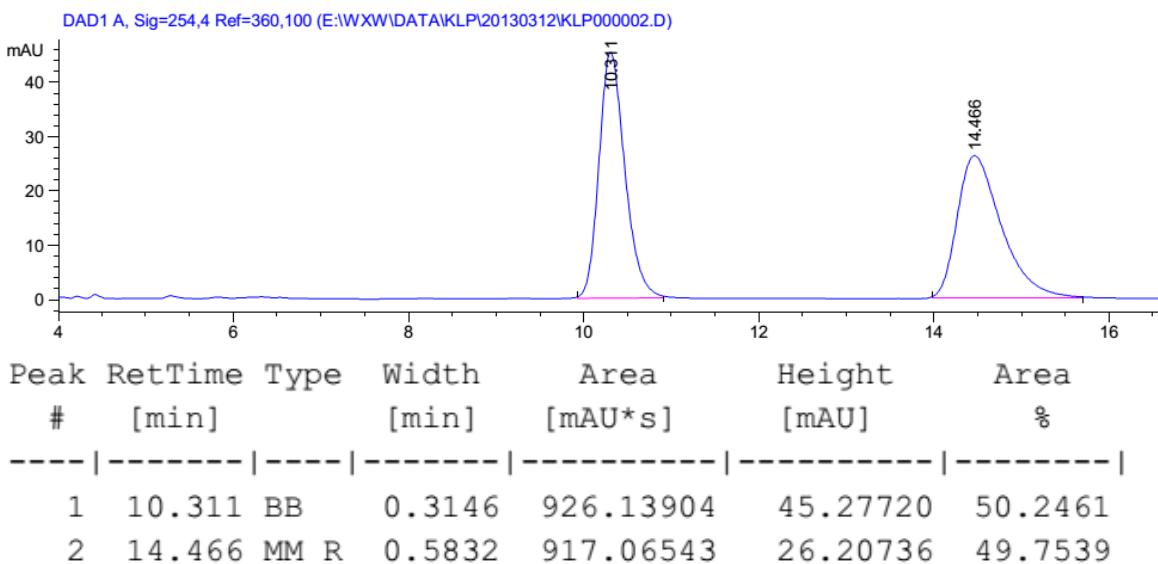


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.372	BB	0.3383	1520.98779	68.68712	49.8918
2	12.072	BB	0.4267	1527.58691	53.88658	50.1082



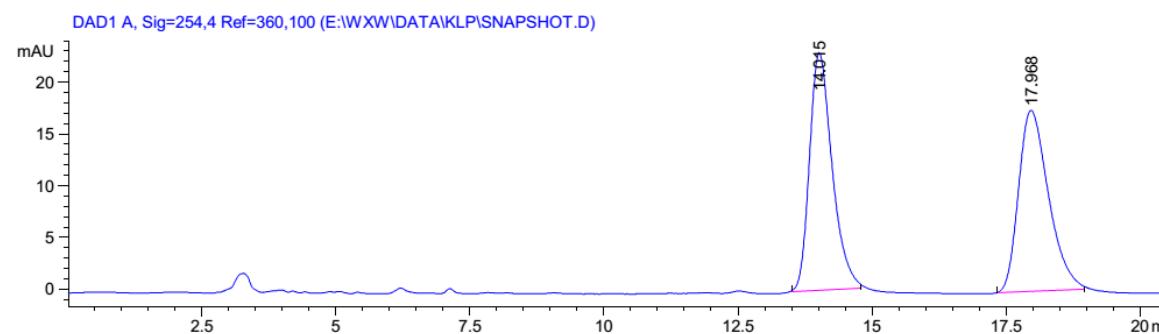
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.348	BB	0.3367	528.65533	24.02961	98.3928
2	12.150	MM R	0.4541	8.63543	3.16952e-1	1.6072

(R)-1-((diphenylphosphoryl)(thiophen-2-yl)methyl)pyrazolidin-3-one (3x)

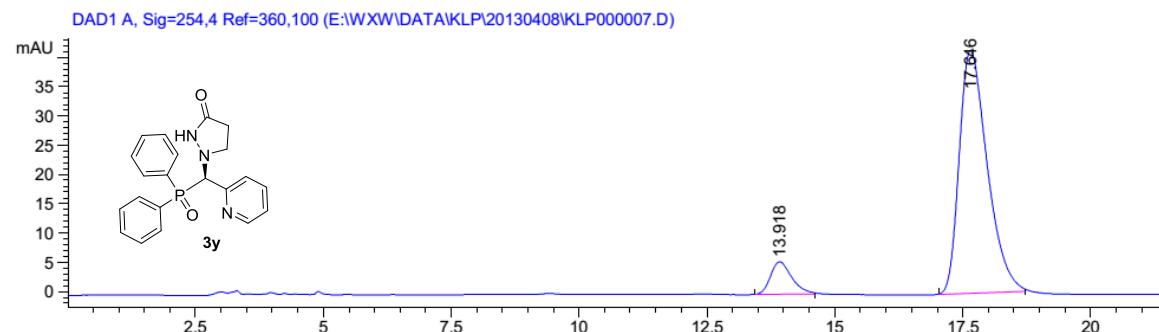


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.342	BB	0.3183	495.78094	23.87268	98.8178
2	14.746	MM R	0.4494	5.93108	2.19952e-1	1.1822

(R)-1-((diphenylphosphoryl)(pyridin-2-yl)methyl)pyrazolidin-3-one (3y)

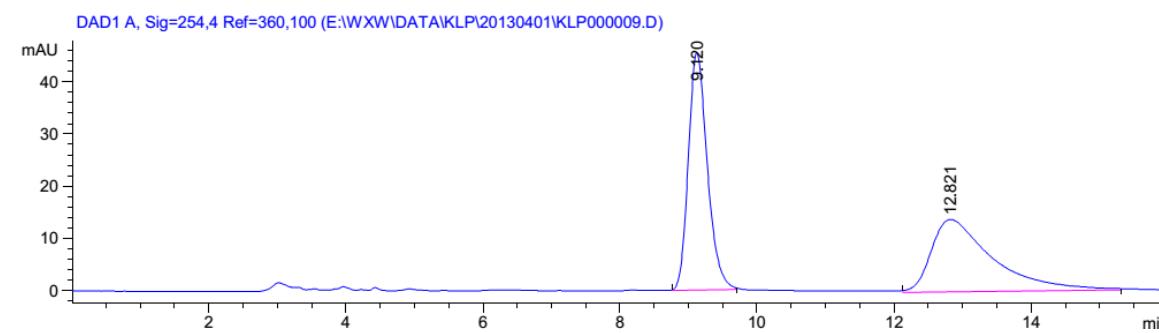


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.015	BB	0.4451	674.82007	22.94798	49.8520
2	17.968	BB	0.5906	678.82562	17.49825	50.1480

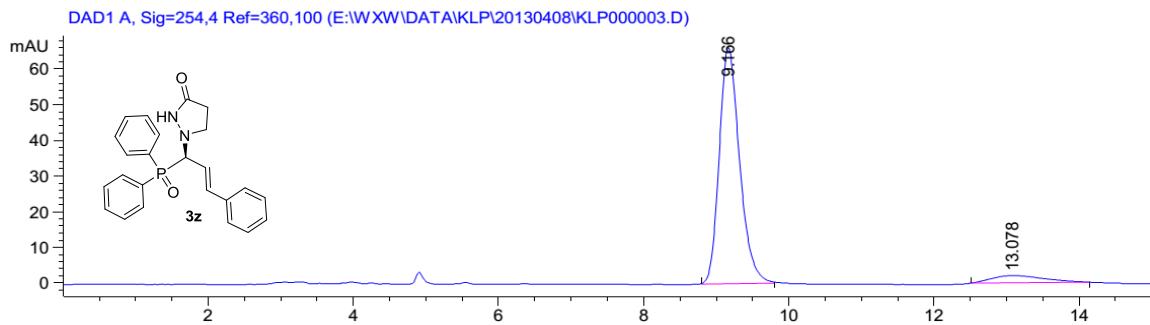


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.918	BB	0.4281	158.36691	5.53071	9.1024
2	17.646	BB	0.5822	1581.47595	41.53578	90.8976

(R,E)-1-(1-(diphenylphosphoryl)-3-phenylallyl)pyrazolidin-3-one (3z)

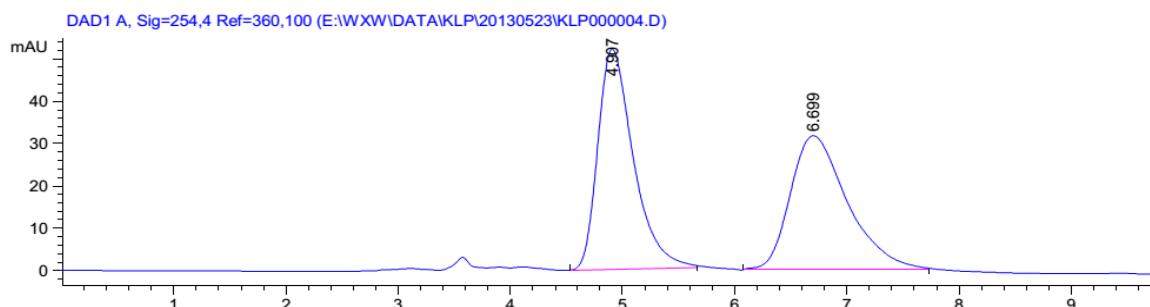


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.120	BB	0.2944	877.30328	45.60379	50.6226
2	12.821	MM R	1.0297	855.72418	13.85063	49.3774

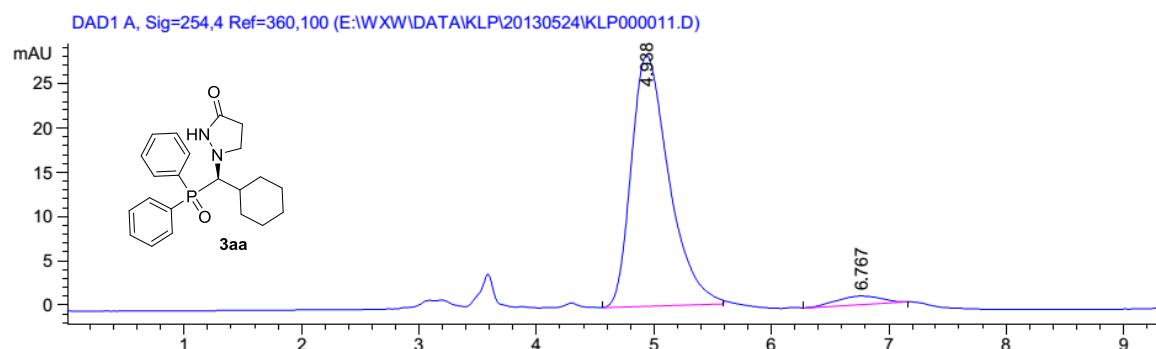


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.166	BB	0.2970	1287.45032	66.17896	92.6585
2	13.078	MM R	0.8450	102.00761	2.01194	7.3415

(R)-1-(cyclohexyl(diphenylphosphoryl)methyl)pyrazolidin-3-one (3aa)

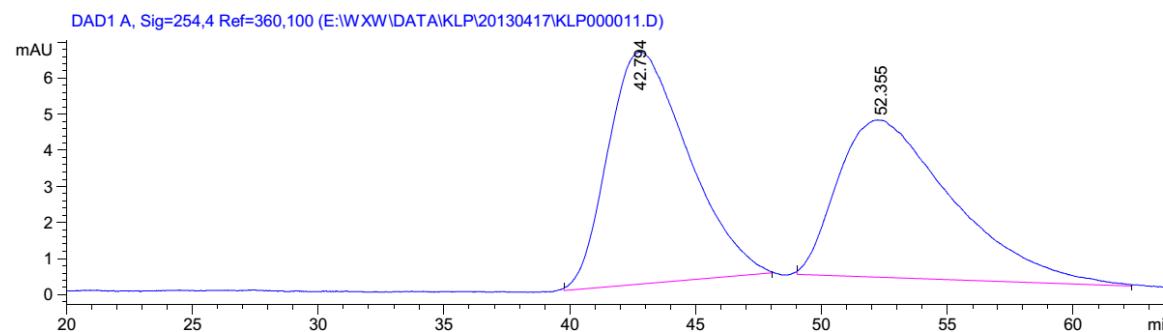


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.907	BB	0.3352	1147.37451	52.04100	50.4890
2	6.699	BB	0.5418	1125.14954	31.71932	49.5110

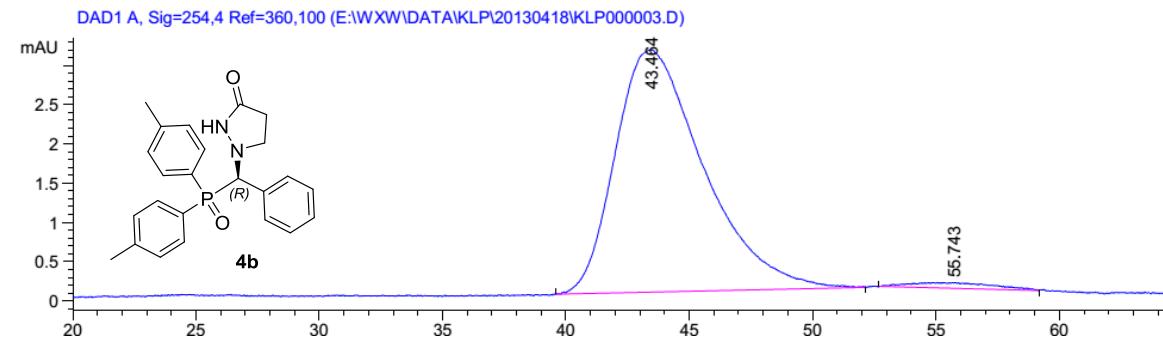


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.938	BB	0.3403	631.98218	28.32361	96.0626
2	6.767	MM R	0.4418	25.90326	9.77146e-1	3.9374

(R)-1-((di-p-tolylphosphoryl)(phenyl)methyl)pyrazolidin-3-one (4b)

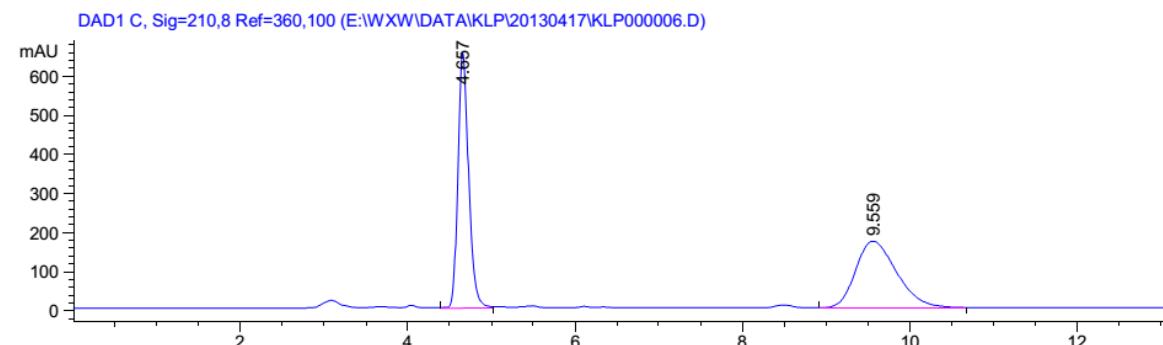


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.794	MM R	3.6899	1424.09570	6.43242	50.8028
2	52.355	MM R	5.2843	1379.08801	4.34967	49.1972



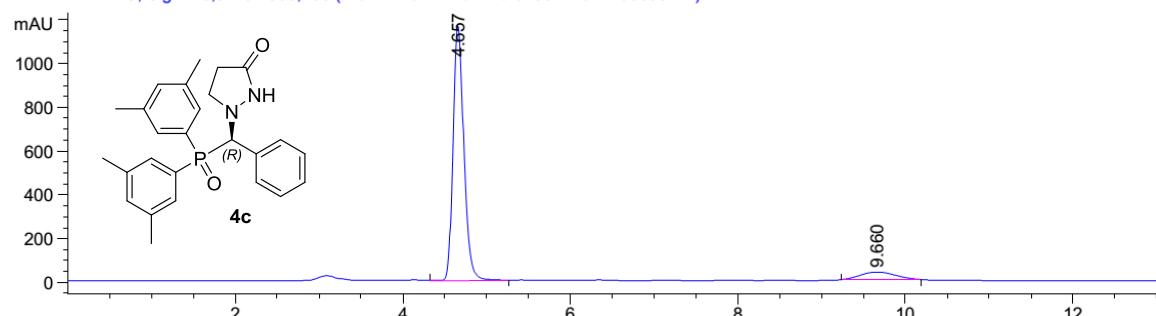
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.464	MM R	4.1395	766.63928	3.08665	97.8354
2	55.743	MM R	3.9727	16.96171	7.11589e-2	2.1646

(R)-1-((bis(3,5-dimethylphenyl)phosphoryl)(phenyl)methyl)pyrazolidin-3-one (4c)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.657	BV	0.1363	5824.80322	651.80316	50.0823
2	9.559	BB	0.5272	5805.65771	170.54573	49.9177

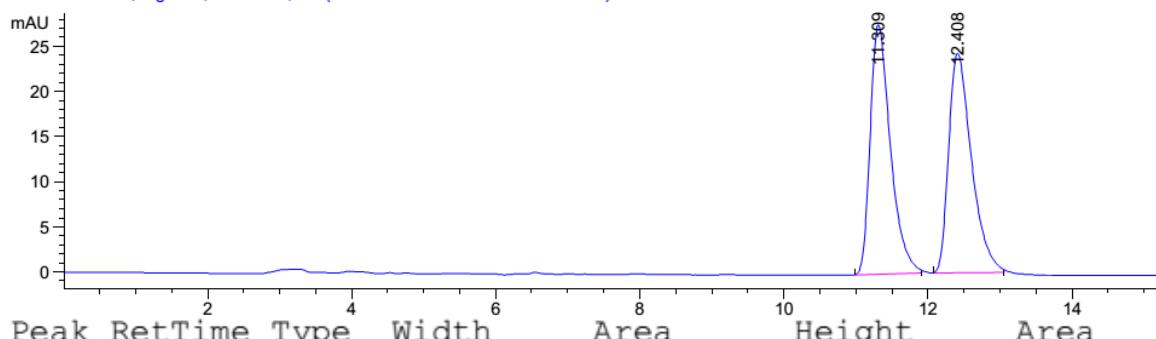
DAD1 C, Sig=210.8 Ref=360,100 (E:\WXW\DATA\KLP\20130417\KLP000007.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.657	VB	0.1394	1.05388e4	1166.98108	91.0588
2	9.660	MM R	0.4910	1034.82166	35.12299	8.9412

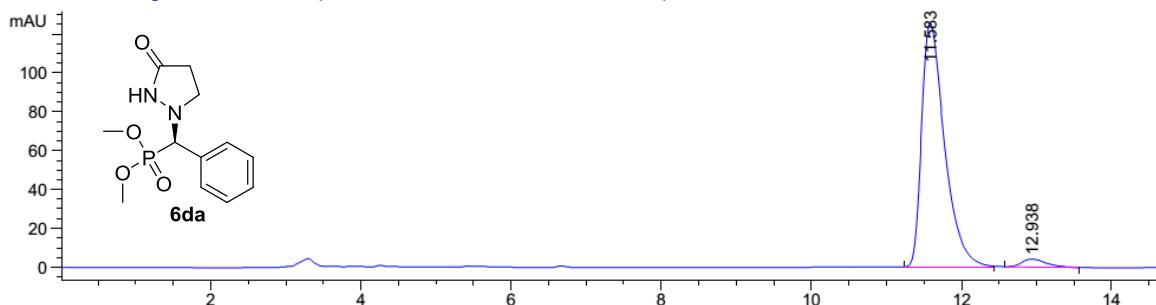
dimethyl (R)-((3-oxopyrazolidin-1-yl)(phenyl)methyl)phosphonate (6da)

DAD1 A, Sig=254.4 Ref=360,100 (E:\WXW\DATA\KLP\SNAPSHOT.D)



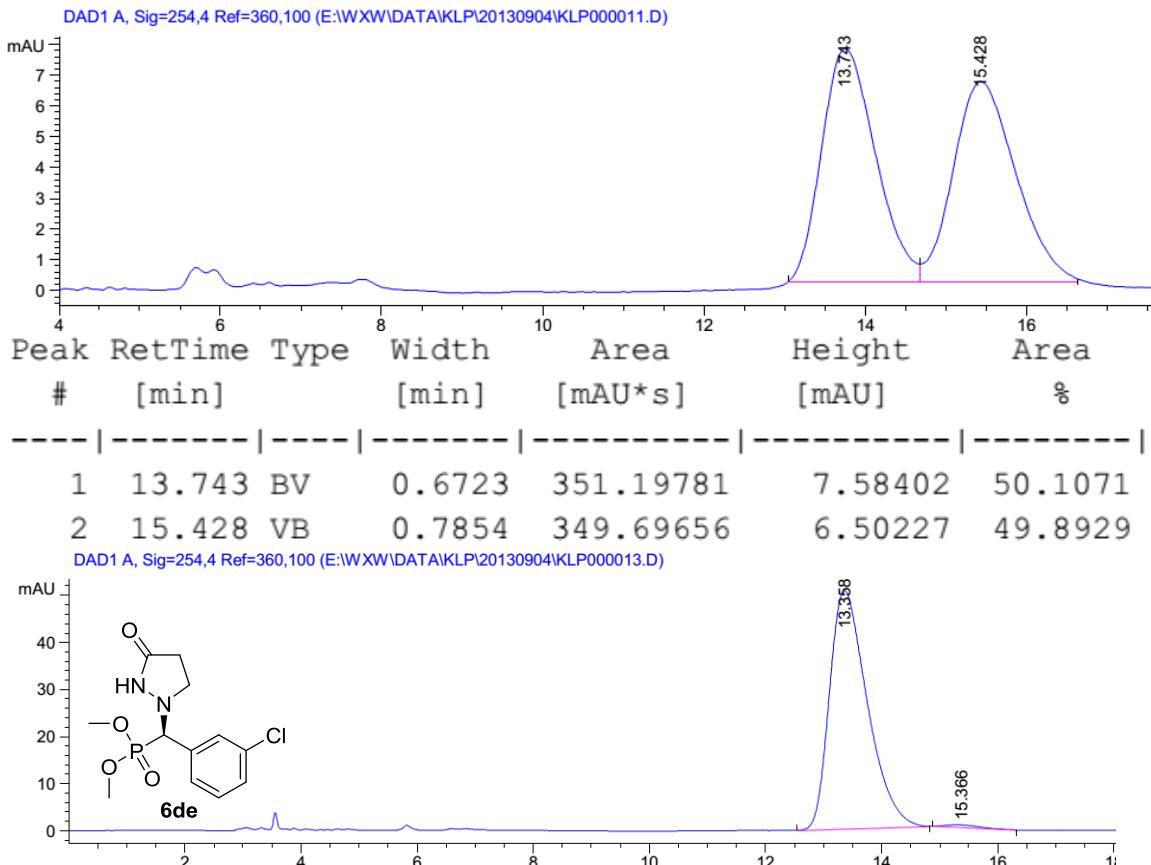
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.309	BB	0.2979	539.51697	27.62028	50.2712
2	12.408	BB	0.3344	533.69586	24.28785	49.7288

DAD1 A, Sig=254.4 Ref=360,100 (E:\WXW\DATA\KLP\20130615\KLP000003.D)

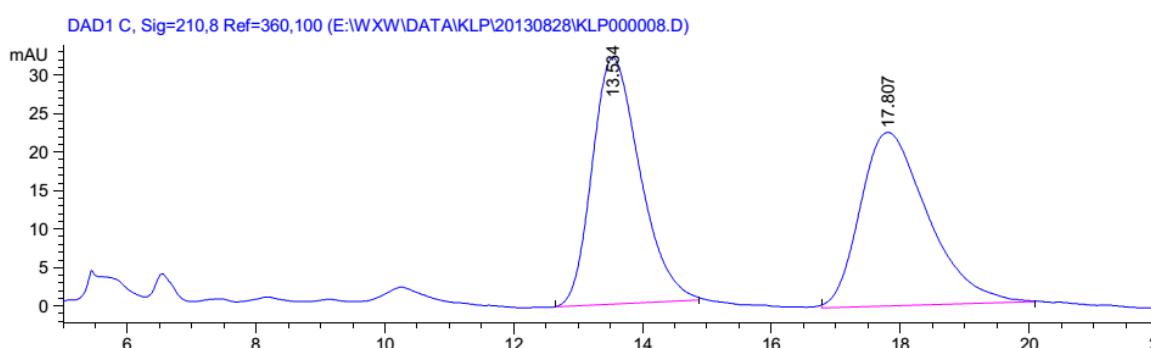


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.583	BB	0.3211	2655.42480	125.39643	96.6054
2	12.938	BB	0.3459	93.30896	4.09400	3.3946

dimethyl (*R*)-((3-chlorophenyl)(3-oxopyrazolin-1-yl)methyl)phosphonate (6de)

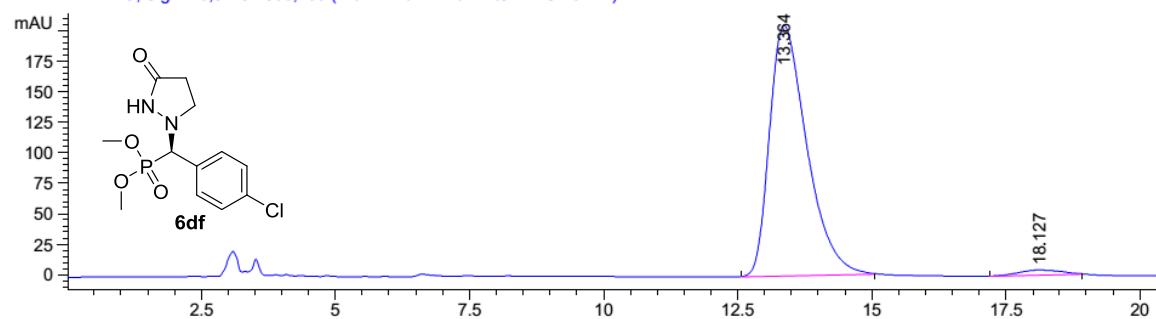


dimethyl (*R*)-((4-chlorophenyl)(3-oxopyrazolin-1-yl)methyl)phosphonate (6df)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.534	BB	0.7864	1647.56580	32.01337	50.1013
2	17.807	MM R	1.2144	1640.90247	22.52030	49.8987

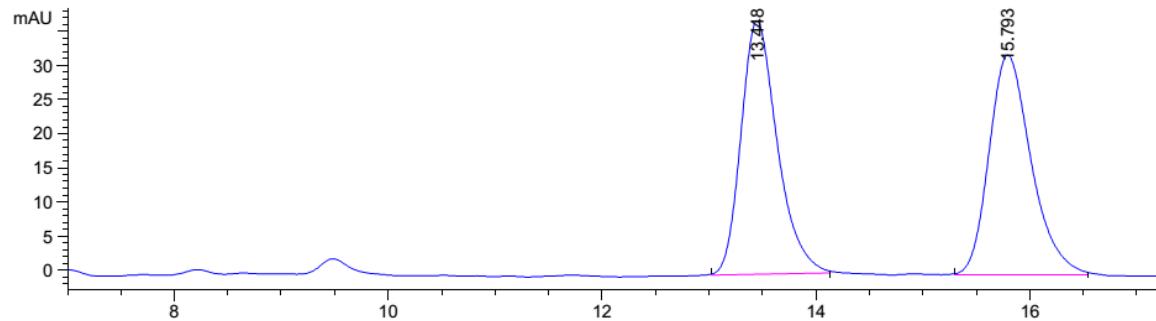
DAD1 C, Sig=210.8 Ref=360,100 (E:\WXW\DATA\KLP\SNAPSHOT.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.364	BB	0.7417	9951.75977	205.23933	97.6350
2	18.127	MM R	0.6824	241.06294	4.21404	2.3650

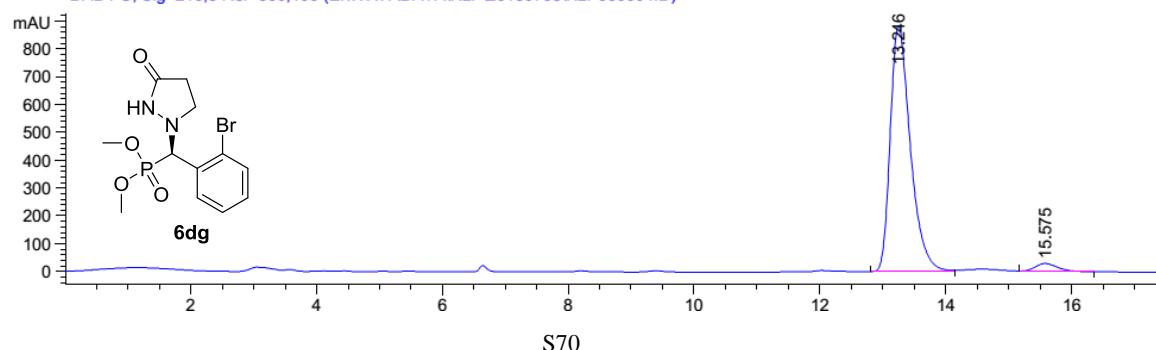
dimethyl (R)-((2-bromophenyl)(3-oxopyrazolin-1-yl)methyl)phosphonate (6dg)

DAD1 C, Sig=210.8 Ref=360,100 (E:\WXW\DATA\KLP\20130608\KLP000007.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.448	BB	0.3609	875.89404	37.16883	49.9391
2	15.793	BB	0.4166	878.03101	32.15467	50.0609

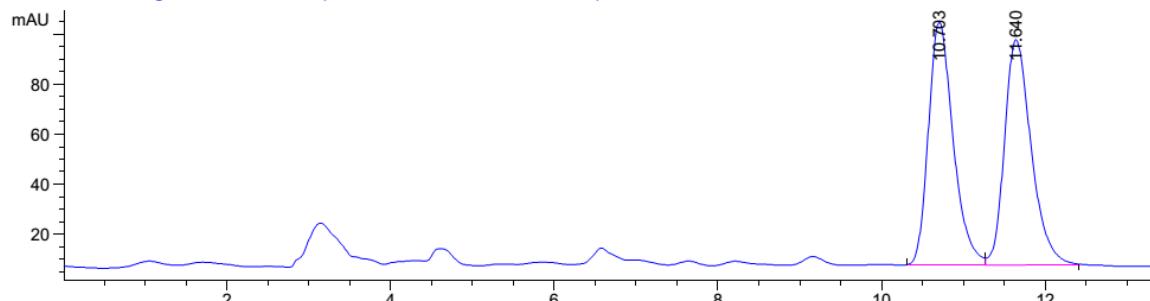
DAD1 C, Sig=210.8 Ref=360,100 (E:\WXW\DATA\KLP\20130703\KLP000004.D)



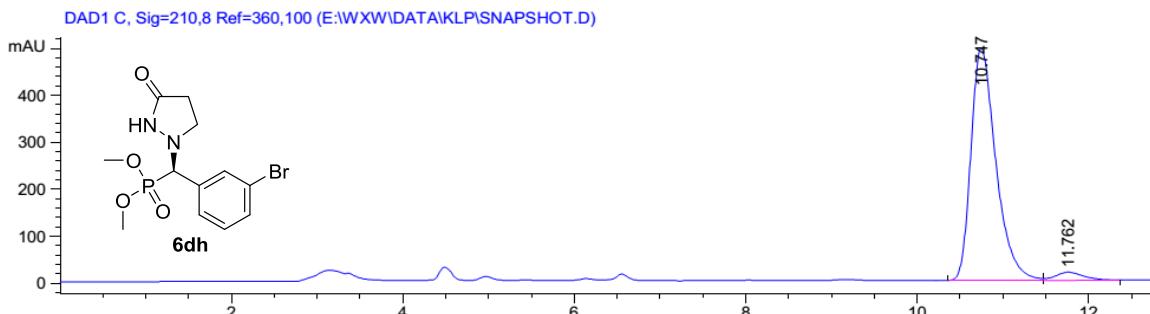
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.246	BB	0.3399	1.97187e4	885.27820	96.0210
2	15.575	VB	0.4069	817.12115	30.27246	3.9790

dimethyl (*R*)-((3-bromophenyl)(3-oxopyrazolin-1-yl)methyl)phosphonate (6dh)

DAD1 C, Sig=210,8 Ref=360,100 (E:\WXW\DATA\KLP\SNAPSHOT.D)



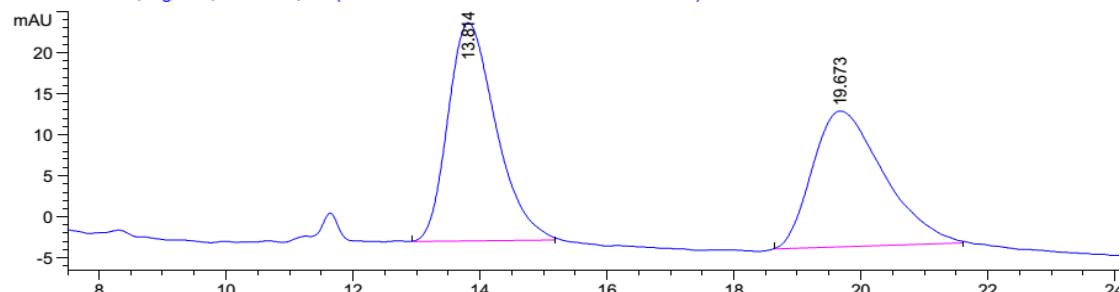
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.703	BV	0.3236	2044.44055	97.10228	49.9858
2	11.640	VB	0.3469	2045.60583	90.10089	50.0142



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.747	BV	0.3099	9998.10742	494.47498	96.1989
2	11.762	VB	0.3462	395.05524	17.05462	3.8011

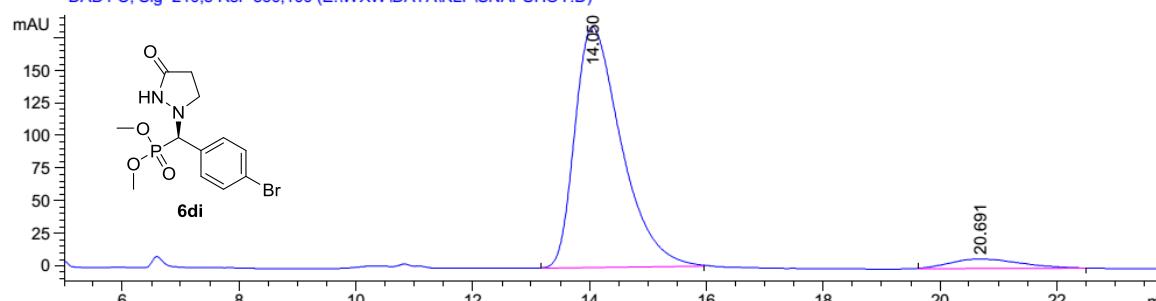
dimethyl (*R*)-((4-bromophenyl)(3-oxopyrazolin-1-yl)methyl)phosphonate (6di)

DAD1 C, Sig=210,8 Ref=360,100 (E:\WXW\DATA\KLP\20130702\KLP00004.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.814	BB	0.7819	1394.11682	26.58089	51.8814
2	19.673	BB	1.0437	1293.00806	16.58307	48.1186

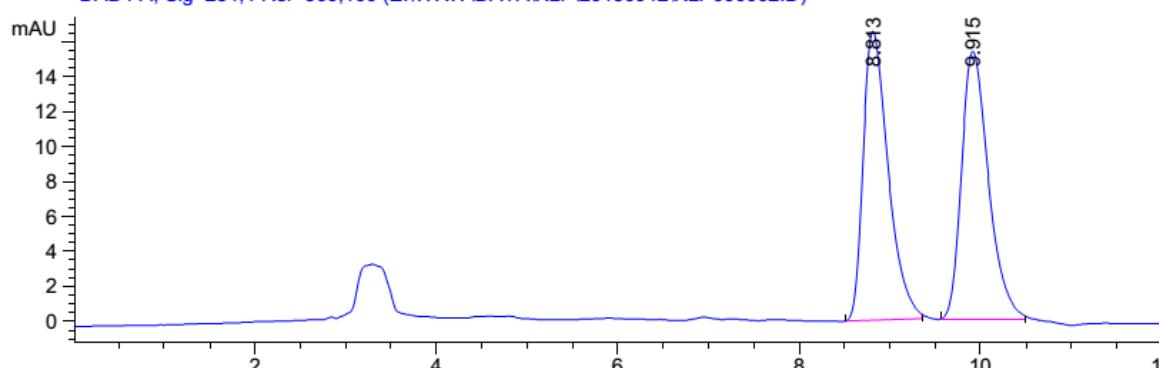
DAD1 C, Sig=210,8 Ref=360,100 (E:\WXW\DATA\KLP\SNAPSHOT.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.050	BB	0.8338	1.02051e4	184.93279	94.3151
2	20.691	BB	0.9896	615.12219	7.35622	5.6849

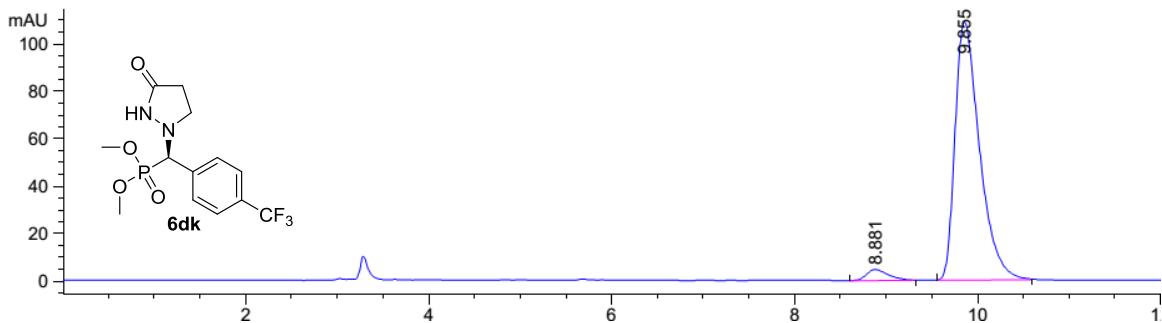
dimethyl (R)-((3-oxopyrazolin-1-yl)(4-(trifluoromethyl)phenyl)methyl)phosphonate (6dk)

DAD1 A, Sig=254,4 Ref=360,100 (E:\WXW\DATA\KLP\20130912\KLP000002.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.813	BB	0.2937	316.80154	16.52094	49.9920
2	9.915	BB	0.3154	316.90286	15.31820	50.0080

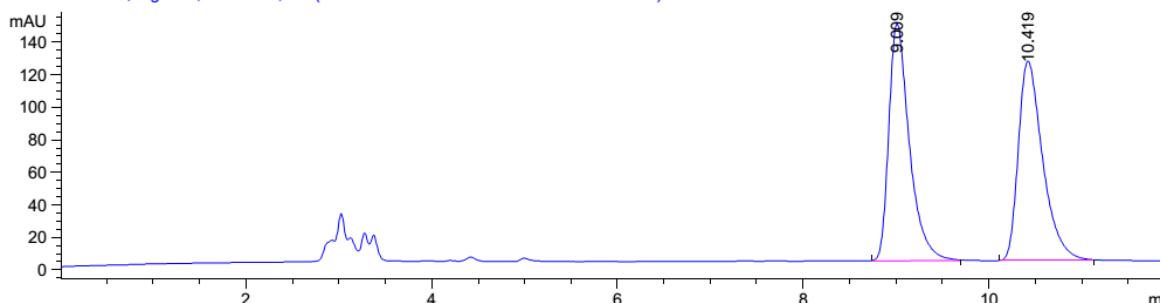
DAD1 A, Sig=254.4 Ref=360,100 (E:\WXW\DATA\KLP\20130912\KLP000006.D)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.881	BB	0.2505	77.12965	4.62648	3.6706
2	9.855	BB	0.2851	2024.16028	108.76174	96.3294

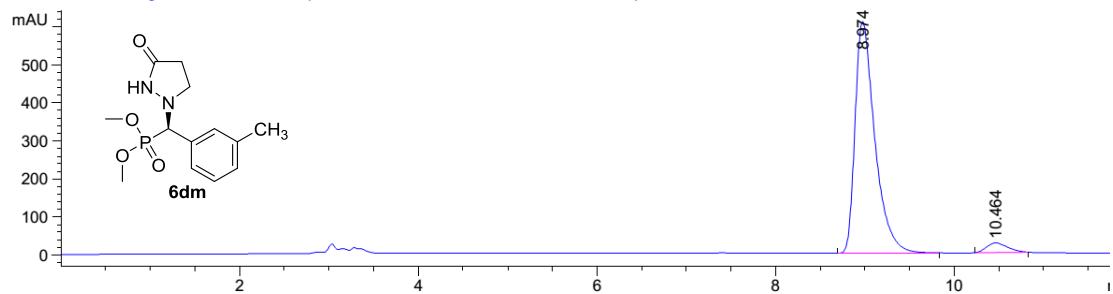
dimethyl (R)-((3-oxopyrazolidin-1-yl)(m-tolyl)methyl)phosphonate (6dm)

DAD1 C, Sig=210.8 Ref=360,100 (E:\WXW\DATA\KLP\20130904\KLP000006.D)



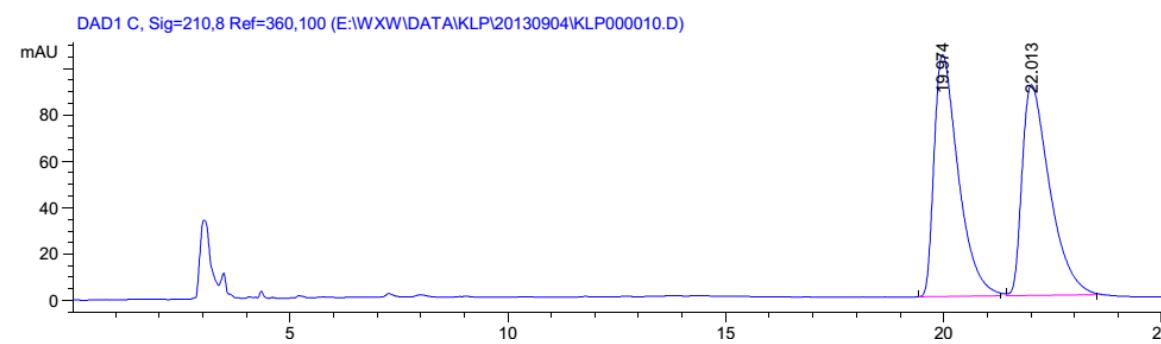
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.009	BB	0.2314	2240.28735	145.69016	50.0119
2	10.419	BB	0.2750	2239.22412	122.62461	49.9881

DAD1 C, Sig=210.8 Ref=360,100 (E:\WXW\DATA\KLP\20130905\KLP000001.D)

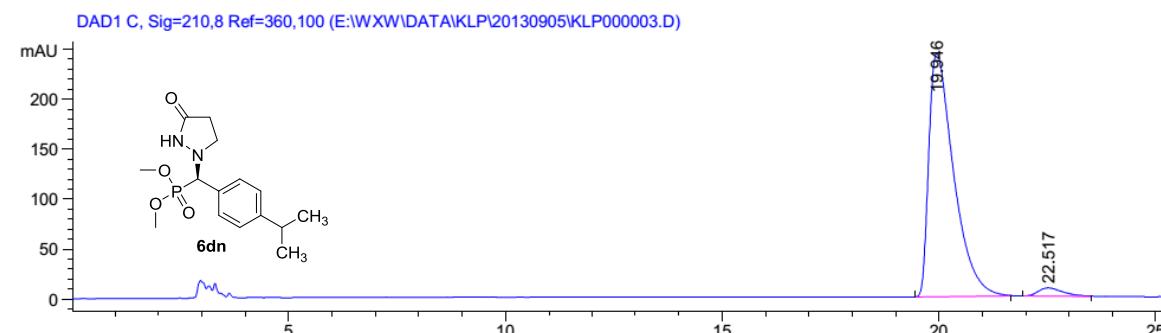


Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.974	BB	0.2314	9354.33789	608.27496	95.8108
2	10.464	MM R	0.2726	409.00711	25.00527	4.1892

dimethyl (R)-((4-isopropylphenyl)(3-oxopyrazolidin-1-yl)methyl)phosphonate (6dn)

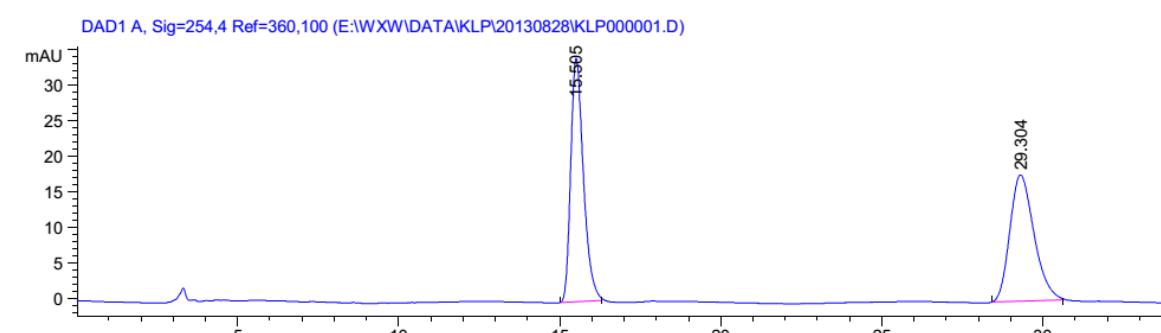


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.974	BB	0.5845	4031.62524	104.41518	50.2025
2	22.013	BB	0.6652	3999.09375	90.90402	49.7975



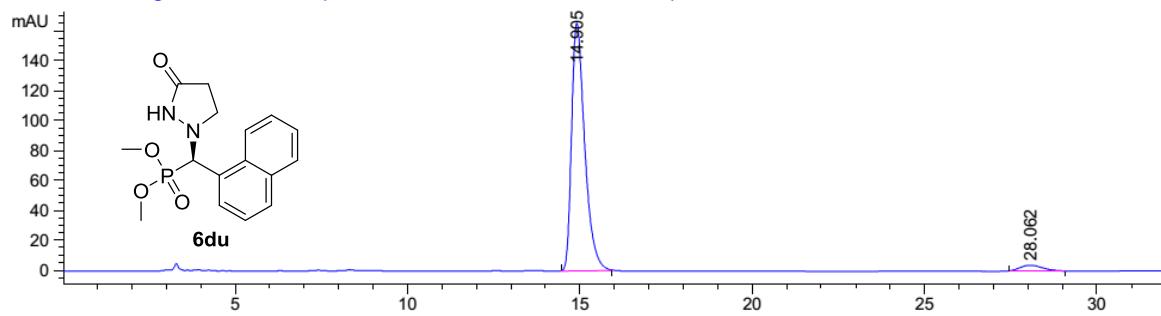
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.946	BB	0.5999	9661.36230	242.98058	96.8066
2	22.517	BB	0.5787	318.70255	8.21337	3.1934

dimethyl (R)-(naphthalen-1-yl(3-oxopyrazolidin-1-yl)methyl)phosphonate (6du)



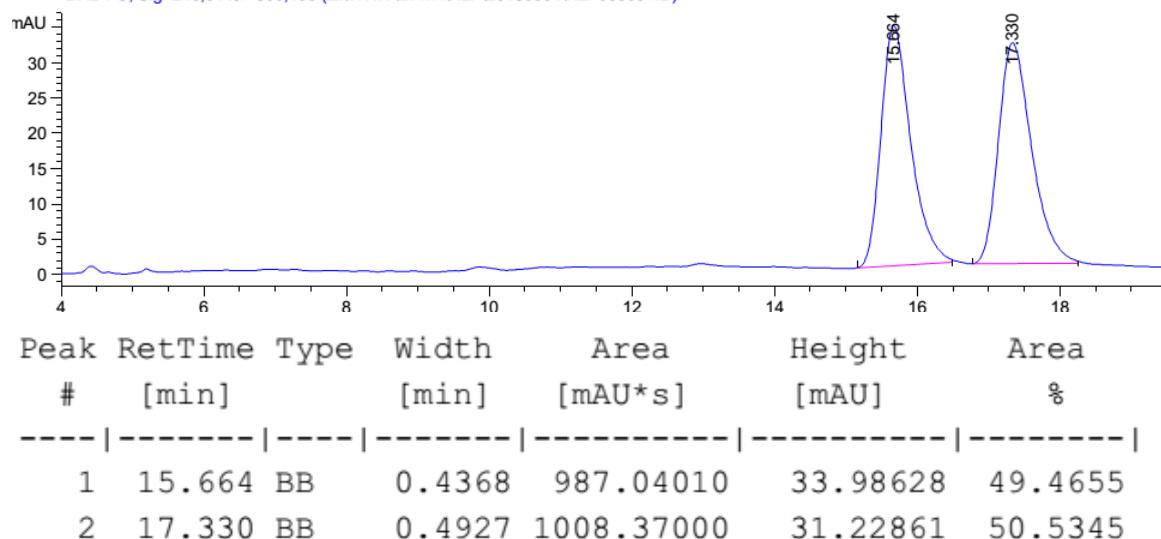
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.505	BB	0.4176	936.74243	34.19100	50.3469
2	29.304	BB	0.7741	923.83459	17.72541	49.6531

DAD1 A, Sig=254.4 Ref=360,100 (E:\WXW\DATA\KLP\20130904\KLP000002.D)

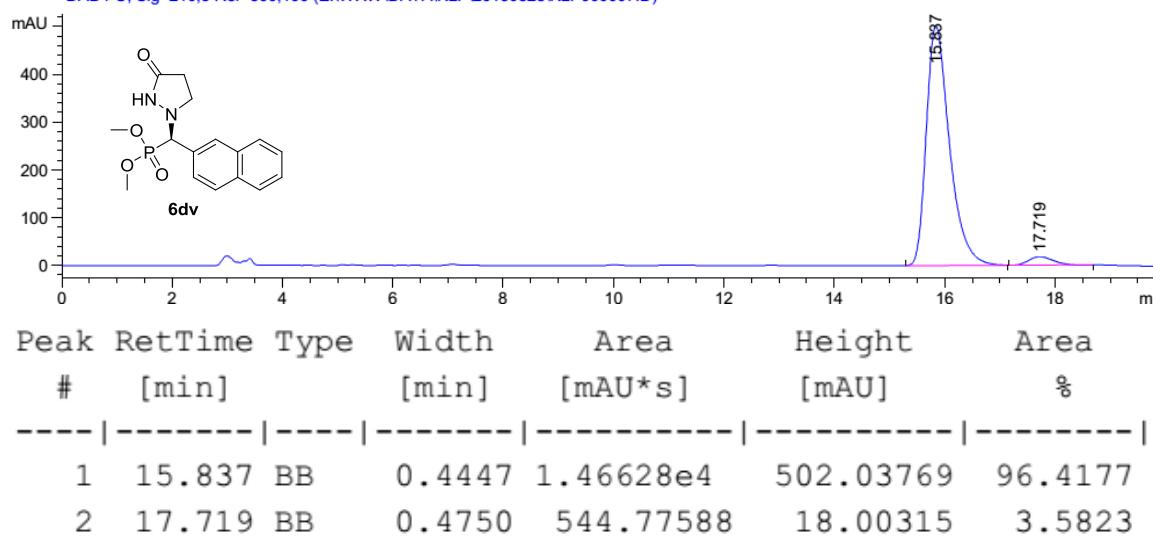


dimethyl (R)-(naphthalen-2-yl(3-oxopyrazolin-1-yl)methyl)phosphonate (6dv)

DAD1 C, Sig=210.8 Ref=360,100 (E:\WXW\DATA\KLP\20130904\KLP000001.D)

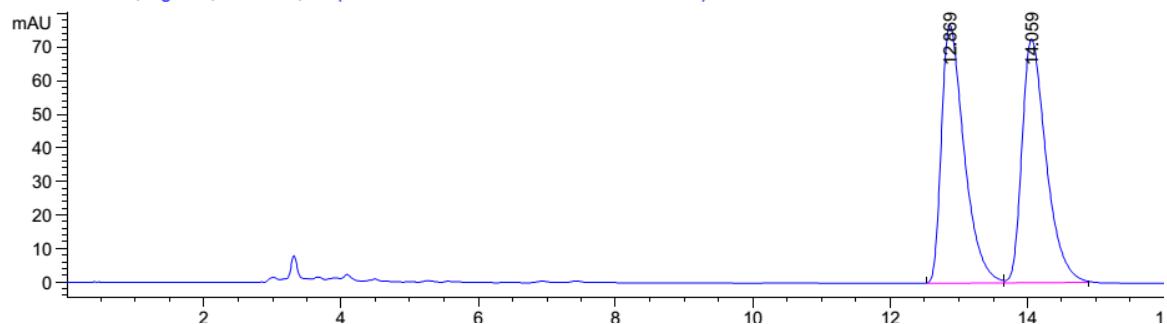


DAD1 C, Sig=210.8 Ref=360,100 (E:\WXW\DATA\KLP\20130828\KLP000007.D)



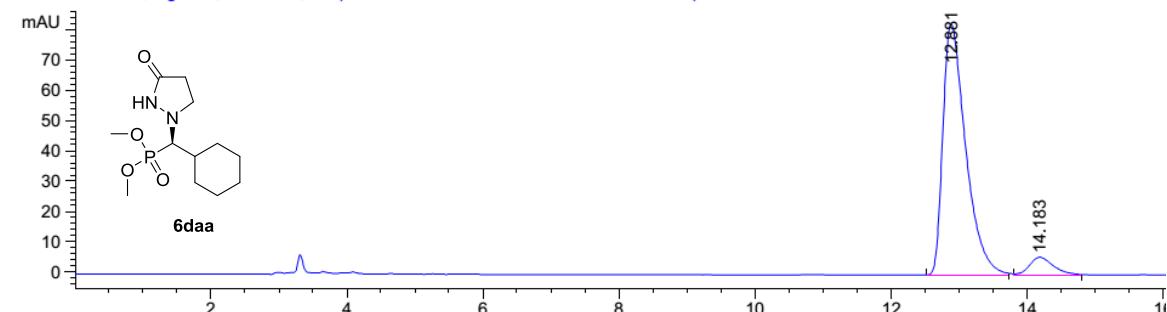
dimethyl (R)-(cyclohexyl(3-oxopyrazolin-1-yl)methyl)phosphonate (6daa)

DAD1 A, Sig=254.4 Ref=360,100 (E:\WXW\DATA\KLP\20130830\KLP000003.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.869	BB	0.3486	1770.65210	76.90829	49.9252
2	14.059	BB	0.3712	1775.95435	72.64226	50.0748

DAD1 A, Sig=254.4 Ref=360,100 (E:\WXW\DATA\KLP\20130830\KLP000004.D)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.881	BB	0.3510	1925.95447	82.92075	93.0813
2	14.183	BB	0.3628	143.15550	5.82315	6.9187