

Supporting Information

Enantioselective Direct Amination of α -Cyanoacetates Catalyzed by Bifunctional Chiral Ru and Ir Amido Complexes

Yasuharu Hasegawa, Masahito Watanabe, Ilya D. Gridnev, and Takao Ikariya*

Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo
Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552 Japan

CONTENTS

1) General experimental procedure	S2
2) Preparation of α -substituted- α -cyanoacetate	S3
3) Experimental procedure for the enantioselective amination of α -substituted- α -cyanoacetate (3) with azodicarboxylate (4) with Ir[(1 <i>S</i> ,2 <i>S</i>)- <i>N</i> -methanesulfonyl-1,2-diphenylethylenediamine](pentamethylcyclopentadienyl) (2a)	S4
4) Determination of absolute configuration of the α -amination product.	S9
5) Stoichiometric reaction of Ir[(1 <i>S</i> ,2 <i>S</i>)- <i>N</i> -methanesulfonyl-1,2-diphenylethylenediamine](pentamethylcyclopentadienyl) (2a) and <i>tert</i> -butyl-2-cyano-2-phenylacetate (3a)	S18
6) Computational details	S22

1) Experimental

General procedure

All manipulation of oxygen and moisture-sensitive materials was conducted under an argon atmosphere by use of standard Schlenk techniques. Solvents were purchased and dried by refluxing over sodium benzophenone ketyl (THF, toluene, diethyl ether), P_2O_5 (CH_2Cl_2 , hexane, CH_3CN), $CaSO_4$ (acetone) and distilled under argon.

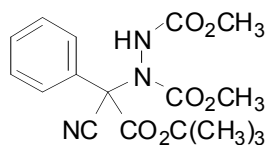
1H , $^{13}C\{^1H\}$ spectra were recorded on a JEOL JNM-LA300. 1H NMR shifts are relative to the signal of the solvent: $CHCl_3$, δ 7.26; $CDHCl_2$, 5.32; $^{13}C\{^1H\}$ NMR shifts are relative to the signal of the solvent: $CDCl_3$, δ 77.00; CD_2Cl_2 , δ 53.5; Peak multiplicities were given as follows: s, singlet; d, doublet; t, triplet; m, multiplet. The coupling constants were described in hertz (Hz). HPLC analyses were conducted on a JASCO PU-980 equipped with a UV-970 detector. IR spectra were recorded on a JASCO FT/IR-610 spectrometer. Mass spectra analyses were performed on a Hitachi M-80B, Thermo Fisher Scientific Polaris Q, and Waters LCT PremierTm XE.

2) Preparation of α -substituted- α -cyanoacetate

Cyanoacetates were prepared by reported procedures (see, Albarella, J. P. *J. Org. Chem.* **1977**, 42, 2009–2010); To a pre-cooled ($-45\text{ }^\circ\text{C}$) mixture of dry THF (100 mL) and dry diisopropylamine (16.56 mL, 117.5 mmol) was added hexane solution of *t*-BuLi (1.58 mol/L, 74.4 mL, 117.5 mmol *t*-BuLi) and stirred for 30 min. Then cyanoacetate (50 mmol) was added dropwisely at $-45\text{ }^\circ\text{C}$ and stirred for another 45 min. Acid anhydride (55 mmol) was finally added and stirred for 1 h at $-45\text{ }^\circ\text{C}$ and allowed to gradually rise up to room temperature and further stirred for 10 h. The mixture was quenched with 20 mL of saturated NH_4Cl . Ether (150 mL) and water (50 mL) was added, and the organic layer was washed with water and brine (each 50 mL x 2). The extracted organic layer was dried over Na_2SO_4 and the product was isolated with column chromatography using silica gel (CH_2Cl_2 or hexane and EtOAc).

3) Experimental procedure for the enantioselective amination of α -substituted- α -cyanoacetate (3) with azodicarboxylate (4) with $Ir[(1S,2S)\text{-}N\text{-methanesulfonyl-1,2-diphenylethylenediamine-pentamethylcyclopentadienyl}]$ (2a)

5a



Under an argon atmosphere, to a toluene solution (5 mL) of **3a** (109 mg, 0.50 mmol) containing the amido catalyst **2a** (3.1 mg, 5 μ mol) was added slowly **4a** (40% toluene solution, 186 μ L, 0.50 mmol) using a syringe pump for 20 minutes at 0 °C. The reaction mixture was then stirred for 2 h at 0 °C. The molar ratio of metal:azodicarboxylate:cyanoacetate is 1:100:100. Since the reaction time for the present amination was influenced by the structures of the reactants, the additional period was required for full conversion of the reactants. After evaporation of the solvent with a vacuum pump, the reaction product was purified with column chromatography (silica gel, eluent: hexane/ethyl acetate) to give the desired adduct **5a** with 95% ee in 99% isolated yield (182 mg). All products **5a–g** being pure compounds give complicated NMR spectra possibly due to the intramolecular dynamics caused by hindered rotation. Details of NMR analysis of the products will be reported in a future publication.

5a: ¹H NMR (300 MHz, CDCl₃, rt, δ /ppm): 1.45, 1.48 (s x 2, 9H, CO₂C(CH₃)₃), 3.50–4.10 (m, 6H, CO₂CH₃ x 2), 6.25, 6.46 (brs x 2, 1H, NH) 7.30–7.90 (m, 5H, C₆H₅). ¹³C{¹H} NMR (75.6 MHz, CDCl₃, rt, δ /ppm): 27.2 (CO₂C(CH₃)₃), 52.8, 54.2, 54.4 (CO₂CH₃ x 2), 69.2 (ArCCN), 85.5 (CO₂C(CH₃)₃), 115.3 (CN), 127.5, 127.9, 128.0, 128.5, 128.8, 128.9, 129.1, 129.4, 130.0, 130.2, 130.3 (C₆H₅), 152.5, 155.4, 155.6, 161.8, 163.2, 163.5 (CO₂C(CH₃)₃, CO₂CH₃ x 2).

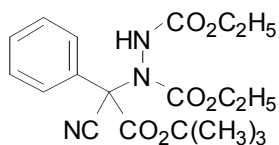
HPLC separation conditions, (column: CHIRALPAK AD (4.6 mm i.d. x 250 mm), eluent: hexane/2-propanol = 90/10, flow rate: 1.0 ml/min, temp: 35 °C, detection: UV 220 nm); retention time of two enantiomers, 11.5 min (minor), 32.4 min (major) MS (CI/isobutane) *m/z* 364 (M + H⁺). [α]_D²⁵ +82.03 (*c* 1.00, CHCl₃).

Table **S1** lists all experimental results obtained from the reaction with chiral Ru catalysts, Ru [(*S,S*)-PMsdpen](η^6 -hmb) (**1a**), Ru [(*S,S*)-Msdpen](η^6 -hmb) (**1b**) Ru [(*S,S*)-Tsdpen](η^6 -hmb) (**1c**) and chiral Ir catalyst **2a–c** (see Scheme 1 in the text).

Table S1. Asymmetric Amination Reaction of α -Substituted α -Cyanoacetates using Azodicarboxylates Catalyzed by Chiral Amido Complexes

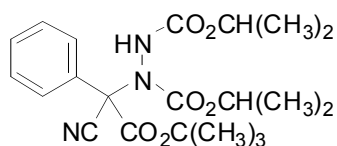
chiral catalyst	cyano- acetate	azo- dicarboxylate	S/C	solvent	temp, °C	product	yield, % ^b	ee, % ^c
–	3a	4a	–	toluene	0	5a	99	–
1a	3a	4a	100	toluene	0	5a	99	66
1b	3a	4a	100	toluene	0	5a	99	34
1c	3a	4a	100	toluene	0	5a	99	13
2a	3a	4a	50	toluene	0	5a	99	94
2a	3a	4a	100	toluene	30	5a	99	90
2a	3a	4a	100	toluene	0	5a	99	95
2a	3a	4a	100	toluene	–30	5a	99	97
2b	3a	4a	100	toluene	0	5a	99	89
2c	3a	4a	100	toluene	0	5a	99	98
2a	3a	4a	100	THF	0	5a	99	83
2a	3a	4a	100	C ₂ H ₅ (CH ₃) ₂ COH	0	5a	99	83
2a	3a	4a	100	acetone	0	5a	99	73
2a	3a	4a	100	CH ₂ Cl ₂	0	5a	99	67
2a	3a	4a	100	CH ₂ Cl ₂	–40	5a	99	92
2a	3a	4a	100	CH ₃ CN	0	5a	99	10
2a	3a	4b	100	toluene	0	5b	99	91
2a	3a	4c	100	toluene	0	5c	99	66
2a	3b	4a	100	toluene	0	5d	99	91
2a	3c	4a	100	toluene	0	5e	99	95
2a	3d	4a	100	toluene	0	5f	99	96
2a	3e	4a	100	toluene	0	5g	99	95

^aUnless otherwise noted, the reaction was carried out by a slow addition of **4** to a solution of **3** containing the amido catalyst with a syringe pump for 20 minutes at 0 °C followed by stirring for 2 h at 0 °C in 5 mL solvent. The molar ratio of metal:azodicarboxylate:cyanoacetate is 1:100:100. ^bIsolated yield after flash chromatography on silica gel. ^cDetermined by HPLC analysis using CHIRALPAK AD (4.6 mm x 250 mm).

5b

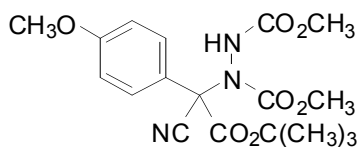
99% yield, 91% ee. ^1H NMR (300 MHz, CDCl_3 , rt, δ/ppm): 1.00–1.75 (m, 15H, $\text{CO}_2\text{CH}_2\text{CH}_3$ x 2, $\text{CO}_2\text{C}(\text{CH}_3)_3$), 3.80–4.40 (m, 4H, $\text{CO}_2\text{CH}_2\text{CH}_3$ x 2), 6.19, 6.39 (brs x 2, 1H, NH), 7.35–7.90 (m, 5H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.6 MHz, CDCl_3 , rt, δ/ppm): 14.1 ($\text{CO}_2\text{CH}_2\text{CH}_3$ x 2), 27.2 ($\text{CO}_2\text{C}(\text{CH}_3)_3$), 61.8, 62.3, 63.7 ($\text{CO}_2\text{CH}_2\text{CH}_3$ x 2), 69.2 (ArCCN), 85.3 ($\text{CO}_2\text{C}(\text{CH}_3)_3$), 115.4 (CN), 127.8, 128.0, 128.4, 128.7, 128.8, 129.3, 129.7, 130.0, 130.2 (C_6H_5), 155.0, 155.1, 163.2, 163.5, ($\text{CO}_2\text{C}(\text{CH}_3)_3$, $\text{CO}_2\text{CH}_2\text{CH}_3$ x 2). See the attached spectrum.

HPLC separation conditions, (column: CHIRALPAK AD (4.6 mm i.d. x 250 mm), eluent: hexane/2-propanol = 90/10, flow rate: 1.0 ml/min, temp: 35 °C, detection: UV 220 nm); retention time of two enantiomers, 11.6 min (minor), 25.7 min (major). $[\alpha]_{\text{D}}^{25}$ +55.89 (*c* 1.00, CHCl_3), MS (CI/isobutane) *m/z* 392 ($\text{M} + \text{H}^+$).

5c

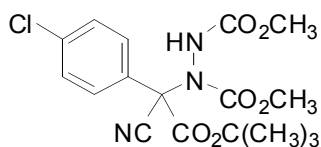
99% yield, 66% ee. ^1H NMR (300 MHz, CDCl_3 , rt, δ/ppm): 0.85–1.50 (m, 21H, $\text{CO}_2\text{CH}(\text{CH}_3)_2$ x 2, $\text{CO}_2\text{C}(\text{CH}_3)_3$), 4.65–5.15 (m, 2H, $\text{CO}_2\text{CH}(\text{CH}_3)_2$ x 2), 5.95, 6.19 (brs x 2, 1H, NH), 7.30–7.80 (m, 5H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.6 MHz, CDCl_3 , rt, δ/ppm): 21.4, 21.5, 21.6, 21.7, 21.8 ($\text{CO}_2\text{CH}(\text{CH}_3)_2$ x 2), 27.4 ($\text{CO}_2\text{C}(\text{CH}_3)_3$), 69.3, 69.8, 70.7, 72.2 ($\text{CO}_2\text{CH}(\text{CH}_3)_2$ x 2, ArCCN), 85.2 ($\text{CO}_2\text{C}(\text{CH}_3)_3$), 115.5, 115.6 (CN), 127.9, 128.0, 128.4, 128.7, 128.9, 129.6, 129.7, 129.9, 130.2 (C_6H_5), 154.3, 154.5, 154.7, 163.3, 163.6 ($\text{CO}_2\text{C}(\text{CH}_3)_3$, $\text{CO}_2\text{CH}(\text{CH}_3)_2$ x 2). See the attached spectrum.

HPLC separation conditions, (column: CHIRALPAK AD (4.6 mm i.d. x 250 mm), eluent: hexane/2-propanol = 90/10, flow rate: 1.0 ml/min, temp: 35 °C, detection: UV 220 nm); retention time of two enantiomers, 10.2 min (minor), 15.8 min (major). MS (CI/isobutane) *m/z* 420 ($\text{M} + \text{H}^+$). $[\alpha]_{\text{D}}^{25}$ +38.17 (*c* 1.00, CHCl_3).

5d

99% yield, 91% ee. ^1H NMR (300 MHz, CDCl_3 , rt, δ /ppm): 1.46, 1.48 (s x 2, 9H, $\text{CO}_2\text{C}(\text{CH}_3)_3$), 3.50–4.00 (m, 9H, CO_2CH_3 x 2, OCH_3), 6.12, 6.36 (brs x 2, 1H, NH), 6.85–7.00 (m, 2H, $\text{C}_6\text{H}_4\text{OCH}_3$), 7.45–7.75 (m, 2H, $\text{C}_6\text{H}_4\text{OCH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.6 MHz, CDCl_3 , rt, δ /ppm): 27.5 ($\text{CO}_2\text{C}(\text{CH}_3)_3$), 53.1, 54.4, 55.3 (OCH_3 , CO_2CH_3 x 2), 68.8 (ArCCN), 85.6 ($\text{CO}_2\text{C}(\text{CH}_3)_3$), 114.0, 114.2, 114.5, 115.7, 120.9, 121.4, 129.2, 129.5, 129.7 ($\text{C}_6\text{H}_4\text{OCH}_3$), 155.6, 160.9, 163.6, 163.9 ($\text{CO}_2\text{C}(\text{CH}_3)_3$, CO_2CH_3 x 2). See the attached spectrum.

HPLC separation conditions, (column: CHIRALPAK AD (4.6 mm i.d. x 250 mm), eluent: hexane/2-propanol = 85/15, flow rate: 1.0 ml/min, temp: 35 °C, detection: UV 220 nm); retention time of two enantiomers, 10.8 min (minor), 36.4 min (major). MS (CI/isobutane) m/z 394 ($\text{M} + \text{H}^+$). $[\alpha]_{\text{D}}^{25} +89.31$ (c 1.00, CHCl_3).

5e

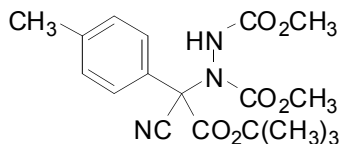
99% yield, 95% ee. ^1H NMR (300 MHz, CDCl_3 , rt, δ /ppm): 1.45, 1.48 (s x 2, 9H, $\text{CO}_2\text{C}(\text{CH}_3)_3$), 3.50–3.90 (m, 6H, CO_2CH_3 x 2), 6.15, 6.39 (brs x 2, 1H, NH), 7.30–7.80 (m, 4H, $\text{C}_6\text{H}_4\text{Cl}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.6 MHz, CDCl_3 , rt, δ /ppm): 27.3 ($\text{CO}_2\text{C}(\text{CH}_3)_3$), 53.1, 53.6, 54.4, 54.5, 54.6 (CO_2CH_3 x 2), 68.8 (ArCCN), 86.0 ($\text{CO}_2\text{C}(\text{CH}_3)_3$), 115.1 (CN), 127.7, 128.2, 128.5, 128.7, 129.1, 129.2, 129.4, 129.5 ($\text{C}_6\text{H}_4\text{Cl}$), 152.6, 155.3, 155.4, 155.6, 155.7, 161.6, 163.0, 163.3 ($\text{CO}_2\text{C}(\text{CH}_3)_3$, CO_2CH_3 x 2). See the attached spectrum.

HPLC separation conditions, (column: CHIRALPAK AD (4.6 mm i.d. x 250 mm), eluent: hexane/2-propanol = 85/15, flow rate: 1.0 ml/min, temp: 35 °C, detection:

UV 220 nm); retention time of two enantiomers, 7.8 min (minor), 21.2 min (major).

MS (CI/isobutane) m/z 398 ($M + H^+$). $[\alpha]_D^{25} +82.66$ (c 1.00, $CHCl_3$).

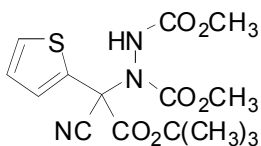
5f



99% yield, 96% ee. 1H NMR (300 MHz, $CDCl_3$, rt, δ/ppm): 1.46, 1.48 (s x 2, 9H, $CO_2C(CH_3)_3$), 2.38 (s, 3H, $C_6H_4CH_3$), 3.50–3.95 (m, 6H, CO_2CH_3 x 2), 6.08, 6.33 (brs x 2, 1H, NH), 7.20–7.80 (m, 4H, $C_6H_4CH_3$). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$, rt, δ/ppm): 21.1 ($C_6H_4CH_3$), 27.5 ($CO_2C(CH_3)_3$), 53.1, 53.7, 54.4, 54.7 (CO_2CH_3 x 2), 69.1 (ArCCN), 85.5 ($CO_2C(CH_3)_3$), 115.6 (CN), 126.2, 126.7, 127.5, 127.9, 128.0, 128.6, 129.3, 129.6, 129.8 ($C_6H_4CH_3$), 155.4, 155.5, 162.1, 163.5, 163.8 ($CO_2C(CH_3)_3$, CO_2CH_3 x 2). See the attached spectrum.

HPLC separation conditions, (column: CHIRALPAK AD (4.6 mm i.d. x 250 mm), eluent: hexane/2-propanol = 90/10, flow rate: 1.0 ml/min, temp: 35 °C, detection: UV 220 nm); retention time of two enantiomers, 11.9 min (minor), 35.3 min (major). MS (CI/isobutane) m/z 378 ($M + H^+$). $[\alpha]_D^{25} +87.08$ (c 1.00, $CHCl_3$).

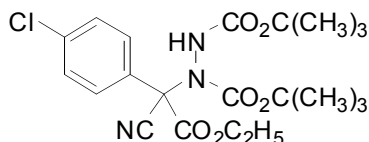
5g



99% yield, 95% ee. 1H NMR (300 MHz, $CDCl_3$, rt, δ/ppm): 1.52 (s, 9H, $CO_2C(CH_3)_3$), 3.60–4.00 (m, 6H, CO_2CH_3 x 2), 6.21, 6.47 (brs x 2, 1H, NH), 6.90–7.10 (m, 1H, C_4H_3S), 7.30–7.75 (m, 2H, C_4H_3S). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$, rt, δ/ppm): 27.5 ($CO_2C(CH_3)_3$), 53.3, 54.5 (CO_2CH_3 x 2), 65.8 (C_4H_3SCCN), 86.2, 86.3 ($CO_2C(CH_3)_3$), 115.0 (CN), 126.8, 127.2, 127.3, 128.6, 129.7, 130.0, 131.1, 131.3, 131.8 (C_4H_3S), 154.8, 155.0, 155.4, 155.7, 163.0, 163.3 ($CO_2C(CH_3)_3$, CO_2CH_3 x 2). See the attached spectrum.

HPLC separation conditions, (column: CHIRALPAK AD (4.6 mm i.d. x 250 mm), eluent: hexane/2-propanol = 90/10, flow rate: 1.0 ml/min, temp: 35 °C, detection: UV 220 nm); retention time of two enantiomers, 10.8 min (minor), 23.7 min (major). MS (CI/methane) m/z 370 ($M + H^+$). $[\alpha]_D^{25} +78.63$ (c 1.00, $CHCl_3$).

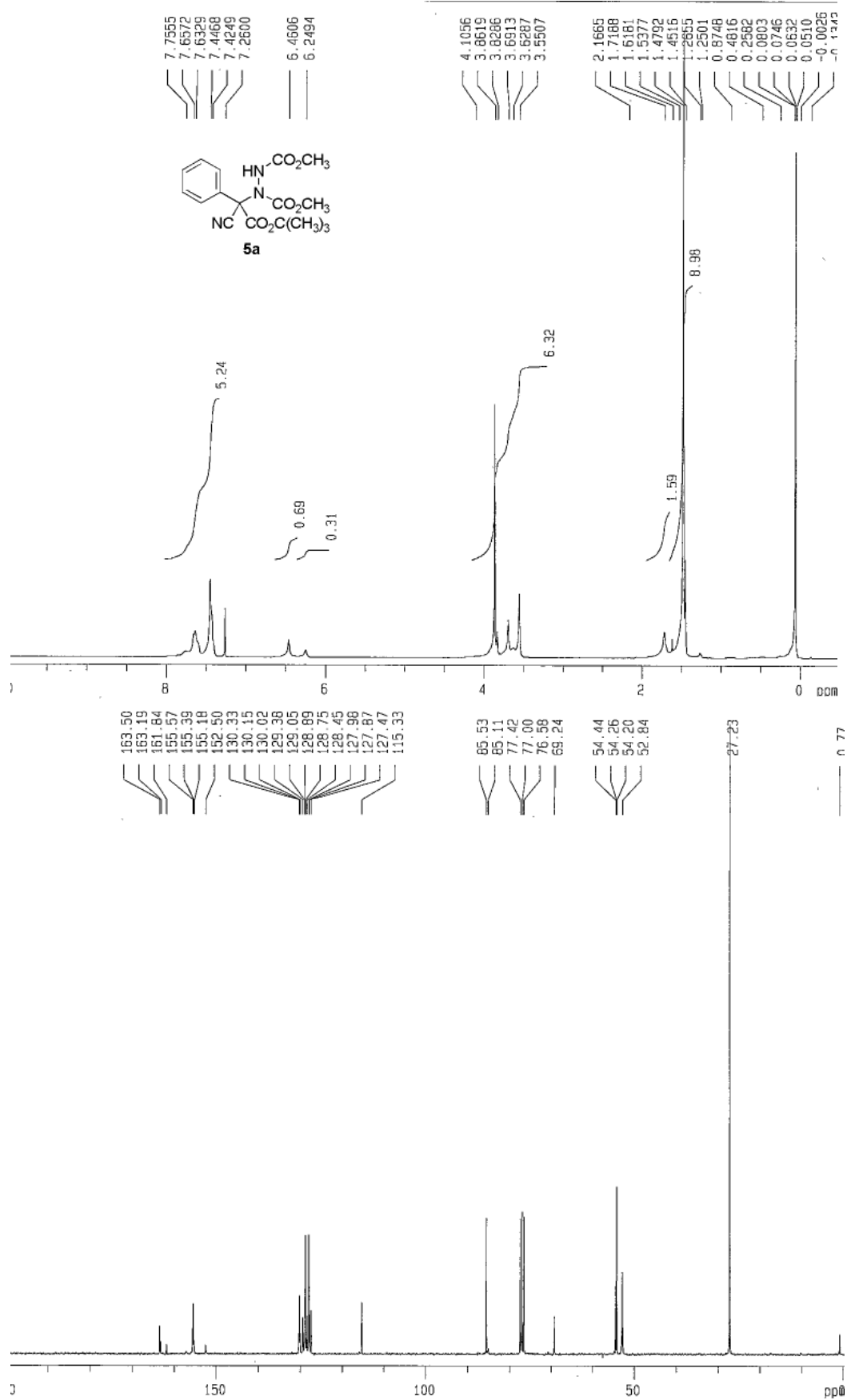
4) Determination of absolute configuration of the α -amination product

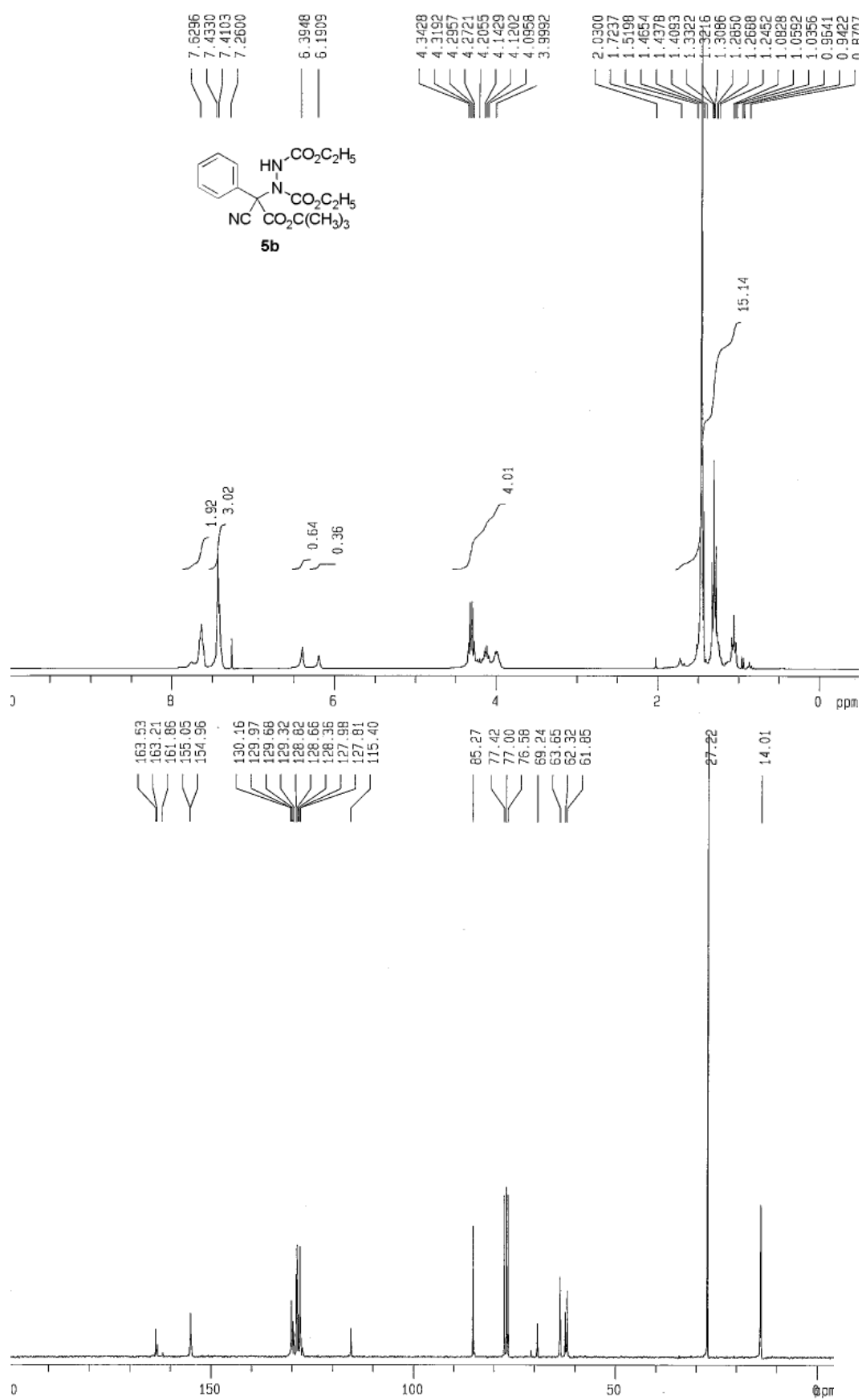


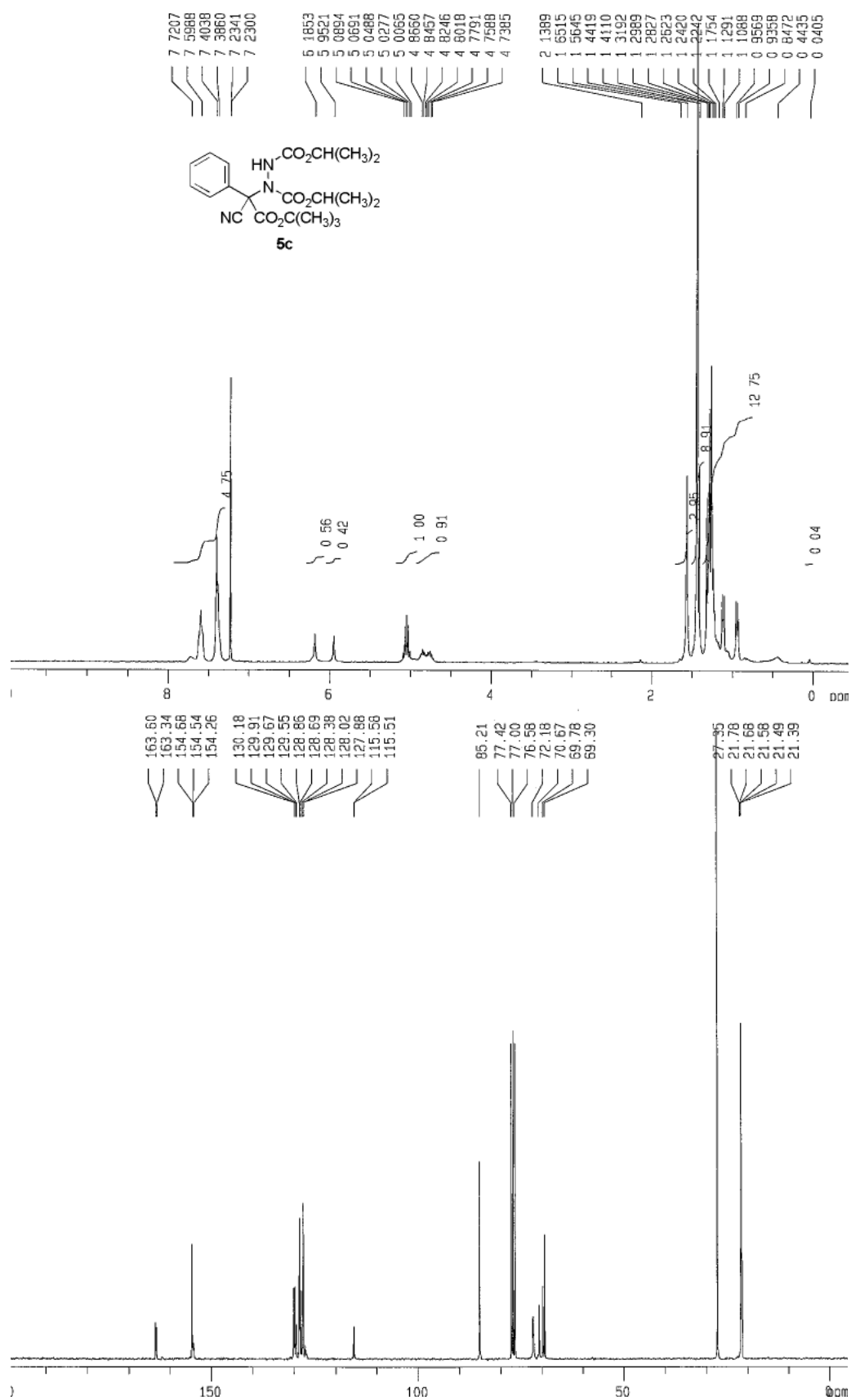
The absolute configuration of the reaction product was determined on the basis of HPLC analysis in comparison to authentic sample (Liu, X.; Li, H.; Deng, L. *Org. Lett.* **2005**, 7, 167–169). The product was identified by comparison of NMR spectrum with the reported compound. The reaction was conducted at –50 °C for 24 h under otherwise the same condition.

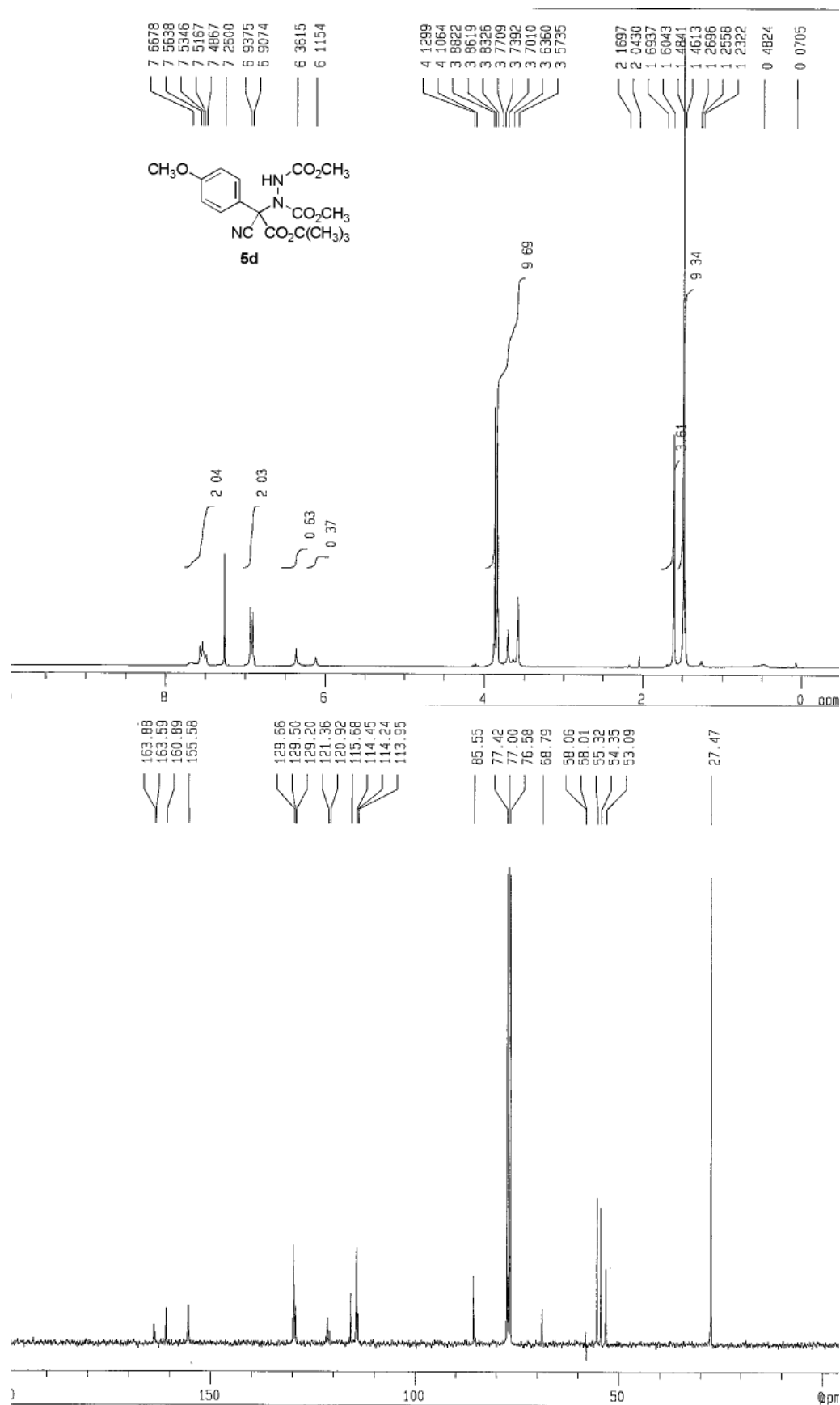
99% yield, 74% ee. 1H NMR (300 MHz, $CDCl_3$, rt, δ /ppm): 1.20–1.90 (m, 21H, $CO_2CH_2CH_3$, $CO_2C(CH_3)_3$ x 2), 4.20–4.50 (m, 2H, $CO_2CH_2CH_3$), 5.80, 6.13 (brs x 2, 1H, NH), 7.30–7.50 (m, 2H, C_6H_4Cl), 7.52–7.80 (m, 2H, C_6H_4Cl). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$, rt, δ /ppm): 13.7 ($CO_2CH_2CH_3$), 27.8, 27.9, 28.1 ($CO_2C(CH_3)_3$ x 2), 64.0 ($CO_2CH_2CH_3$), 68.5 (ArCCN), 81.8, 83.3, 84.6 ($CO_2C(CH_3)_3$ x 2), 115.4 (CN), 128.3, 128.7, 128.9, 129.0, 129.4, 129.6, 136.2, 136.4, 136.8 (C_6H_4Cl), 154.1, 164.8, 165.1 ($CO_2C(CH_3)_3$ x 2, $CO_2C_2H_5$). See the attached spectrum.

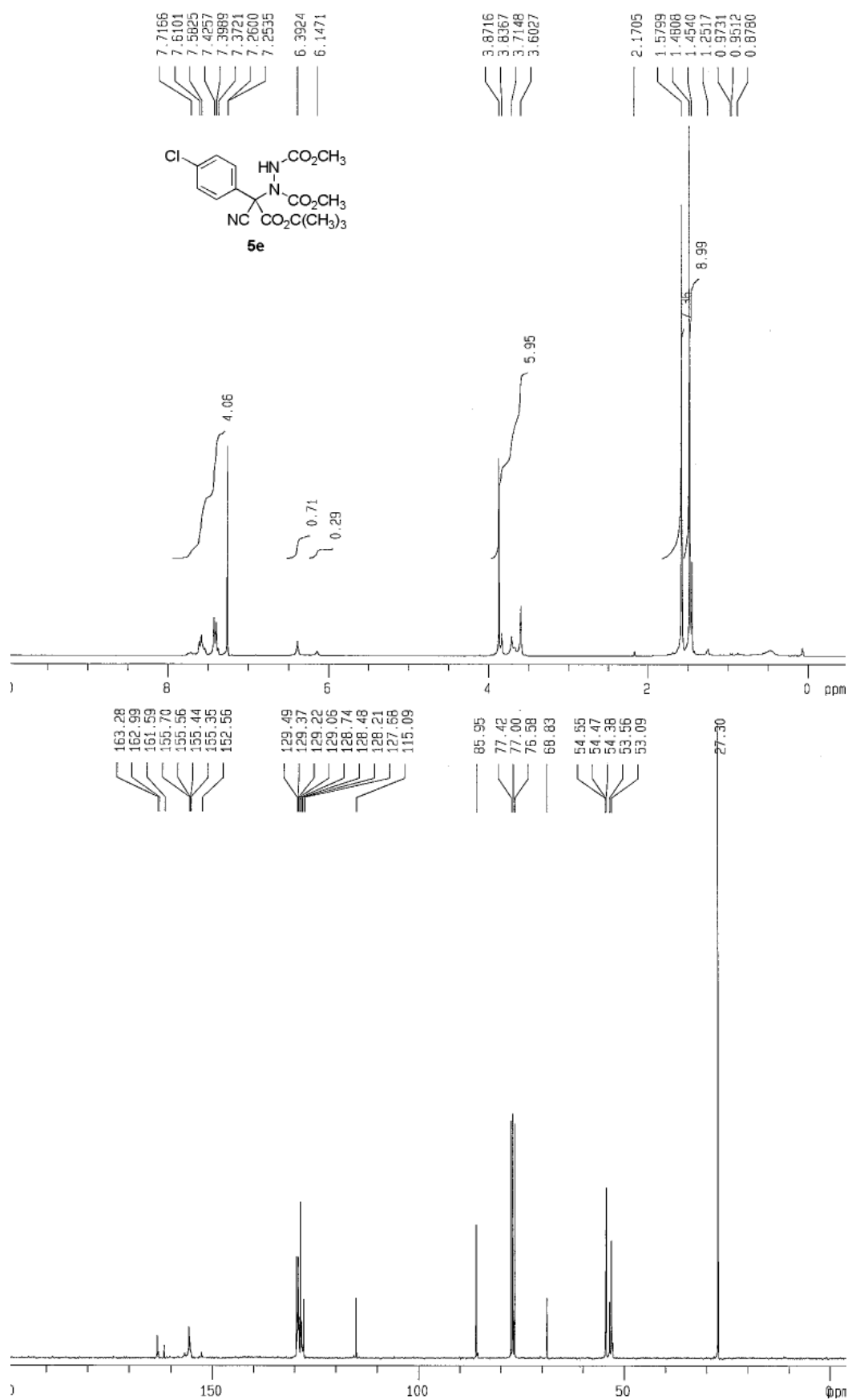
HPLC separation conditions, (column: CHIRALPAK AD (4.6 mm i.d. x 250 mm), eluent: hexane/2-propanol = 90/10, flow rate: 1.0 ml/min, temp: 35 °C, detection: UV 220 nm); retention time of two enantiomers, 14.9 min (minor), 23.4 min (major). HRMS $C_{21}H_{28}ClN_3O_6$ [$M + H^+$] ; calcd. 454.1745, found 454.1745. $[\alpha]_D^{25} +49.6$ (c 1.00, $CHCl_3$), *R* configuration.

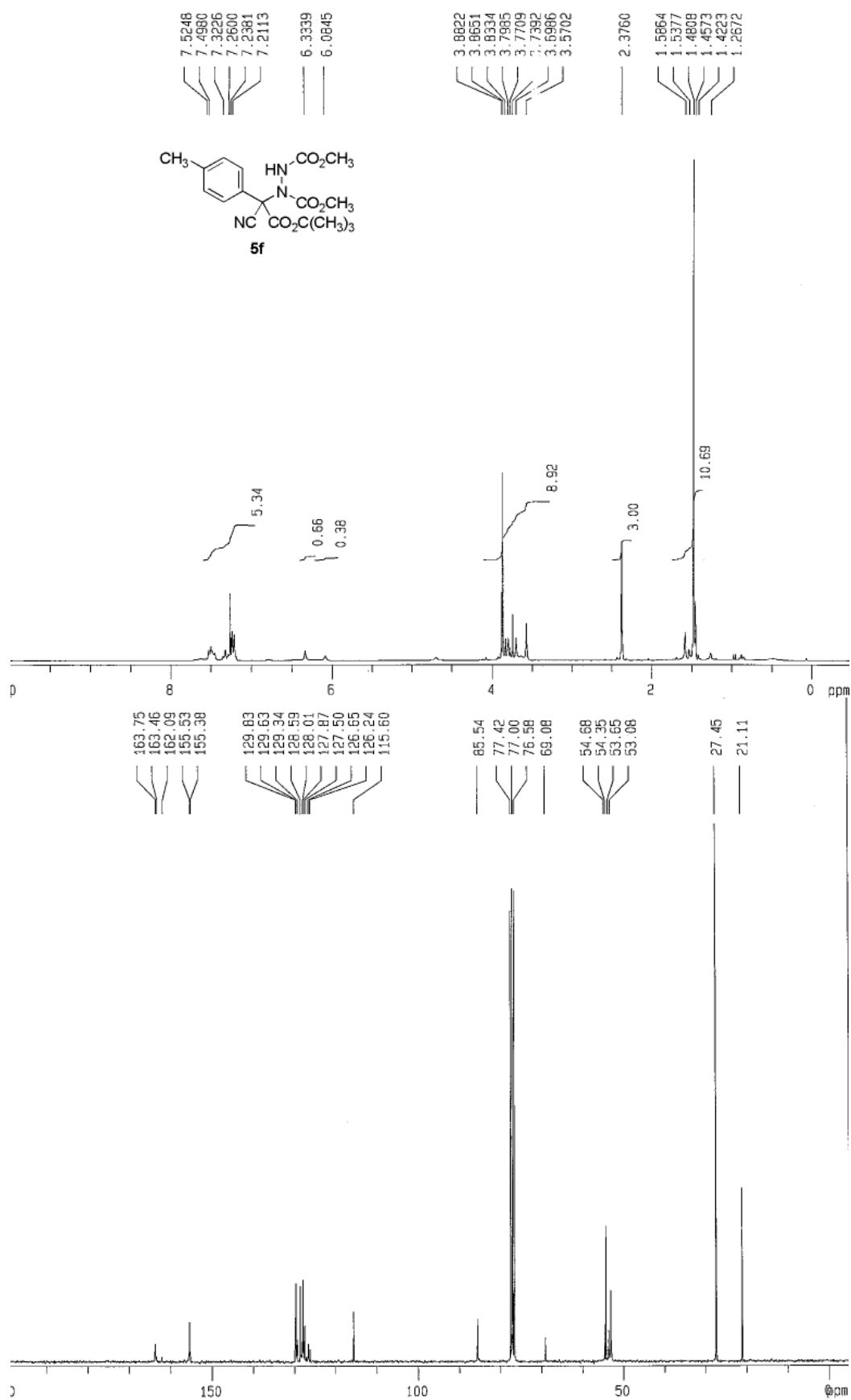


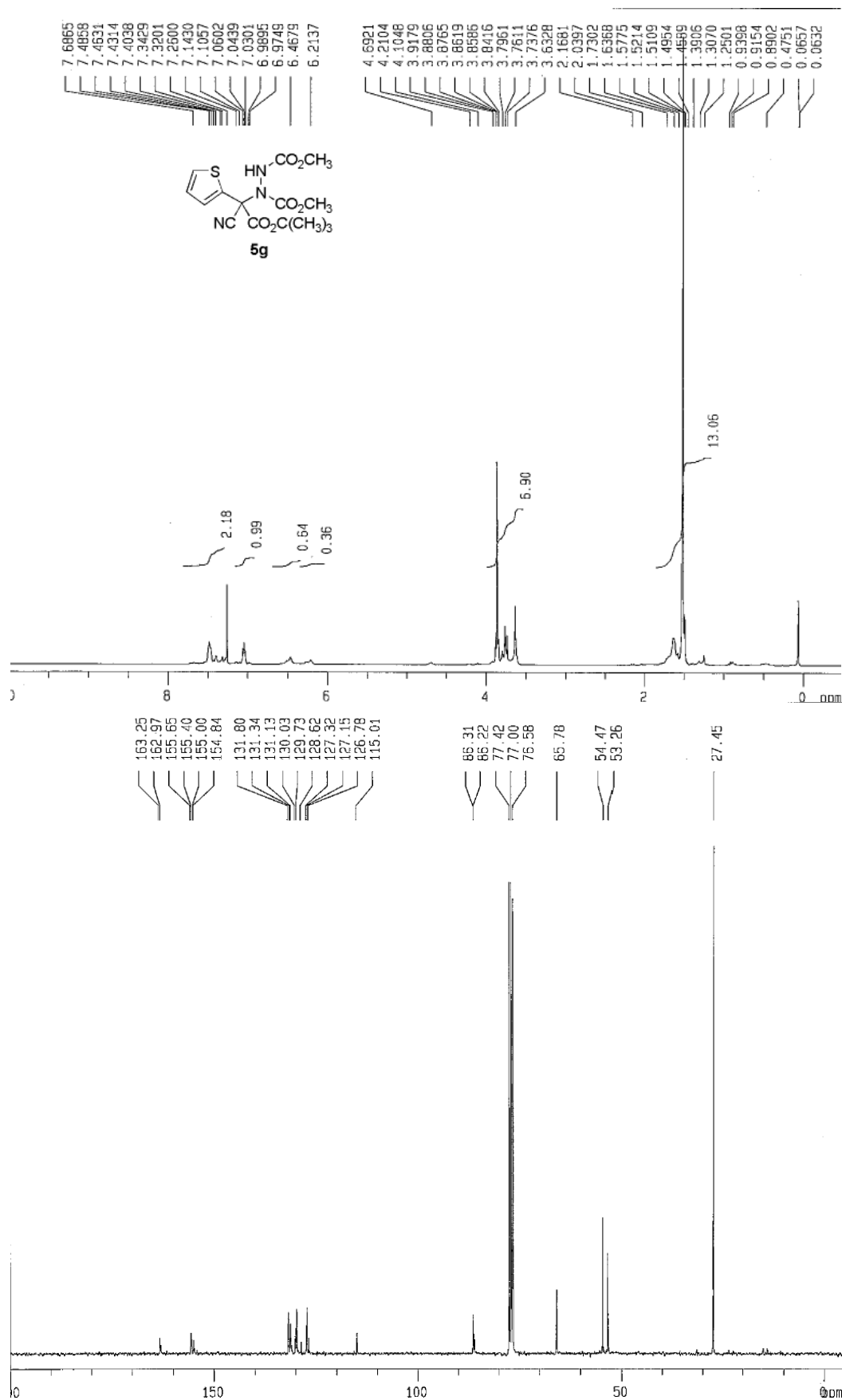


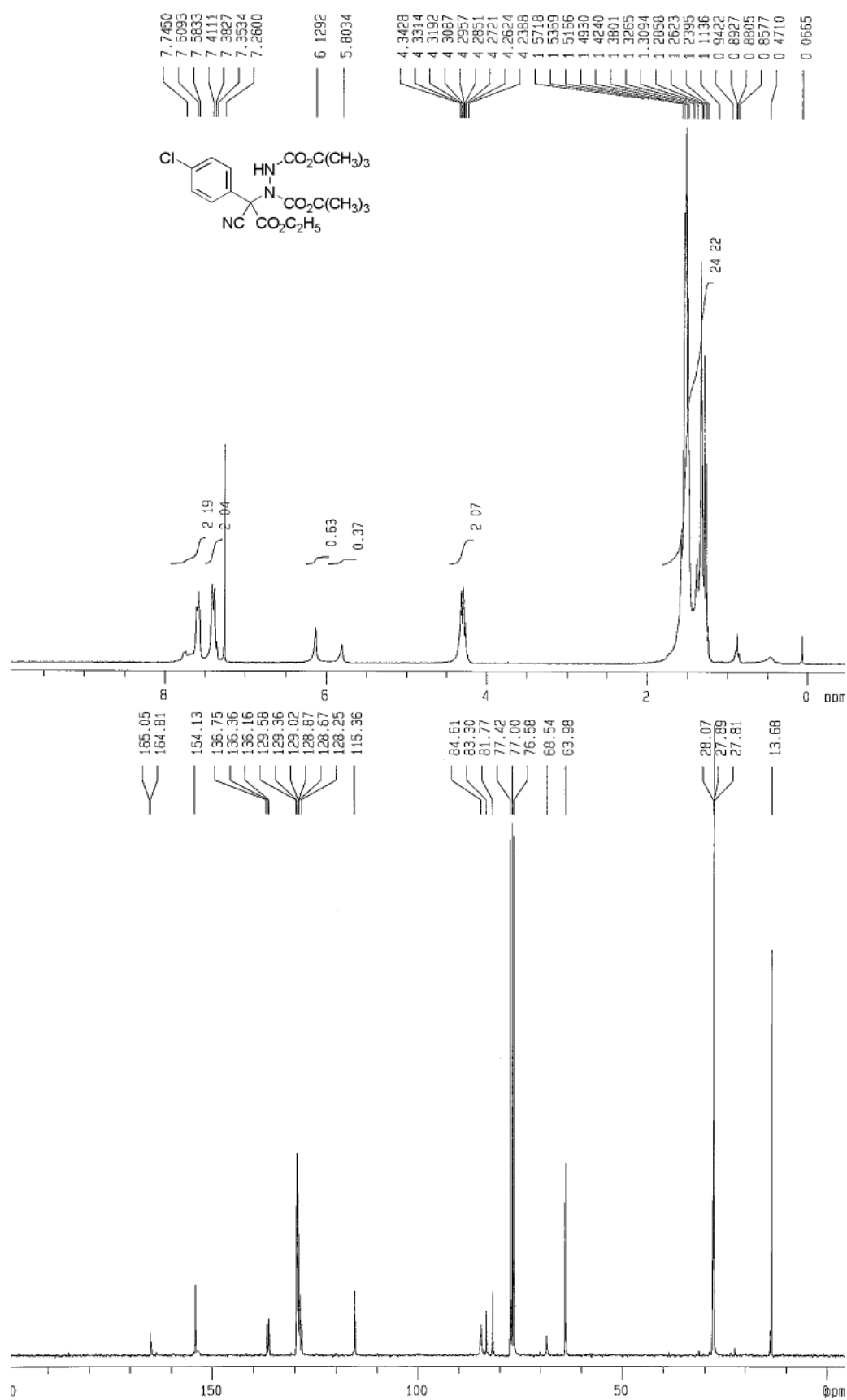




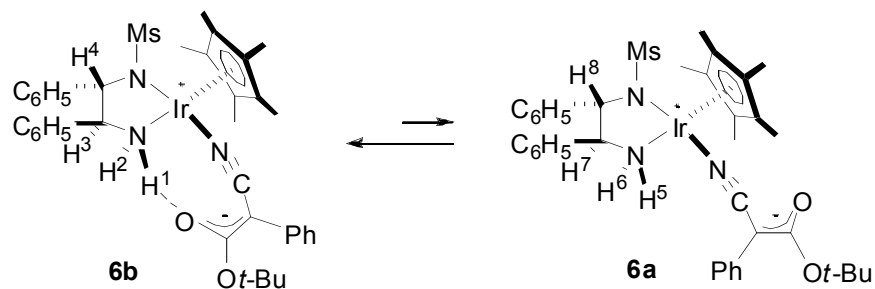








5) Stoichiometric reaction of Ir[(1*S*,2*S*)-*N*-methanesulfonyl-1,2-diphenylethylenediamine](pentamethylcyclopentadienyl) (2a**) and *tert*-butyl-2-cyano-2-phenylacetate (**3a**)**



2a:3a = 1:1.5 in molar ratio. (Free cyanoacetate was also present in the spectrum.) ^1H NMR (300 MHz, CDCl_3 , -50°C , δ/ppm): 1.19 (s, $\text{C}_5(\text{CH}_3)_5$ of **6a** and **6b**), 1.57 ($\text{CO}_2\text{C}(\text{CH}_3)_3$ of free cyanoacetate), 1.76 (s, $\text{CO}_2\text{C}(\text{CH}_3)_3$ of **6a** and **6b**), 2.12 (CH_3SO_2 of **6a**), 2.22 (CH_3SO_2 of **6b**), 3.68–3.76 (m, H^3 , H^7), 4.02 (t, $J = 11.5$ Hz, H^5), 4.22 (d, H^2), 4.46–4.54 (m, H^6 , H^4 , H^8), 4.68 (d, $J = 3.4$ Hz, CHCN of free cyanoacetate), 6.22 (t, H^1), 6.73–7.77 (m, 3 phenyls of **6a** and **6b**, 1 phenyl from free cyanoacetate). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.6 MHz, CD_2Cl_2 , -50°C , δ/ppm): 8.9 ($\text{C}_5(\text{CH}_3)_5$ of **6a** and **6b**), 26.8 ($\text{C}(\text{CH}_3)_3$ of **6a** and **6b**), 28.3 ($\text{C}(\text{CH}_3)_3$ of free cyanoacetate), 42.1 (CH_3S of **6a**), 43.2 (CH of free cyanoacetate), 44.2 (CH_3S of **6b**), 58.6 (PhC^-CN of **6b**), 68.1, 74.1 ($\text{CHPh} \times 2$ of **6b**), 68.7, 73.4 ($\text{CHPh} \times 2$ of **6a**), 76.2 ($\text{C}(\text{CH}_3)_3$ of **6a**), 78.2 ($\text{C}(\text{CH}_3)_3$ of **6b**), 84.1 ($\text{CO}_2\text{C}(\text{CH}_3)_3$ of free cyanoacetate), 86.3 ($\text{C}_5(\text{CH}_3)_5$ of **6b**), 86.6 ($\text{C}_5(\text{CH}_3)_5$ of **6a**), 116.0 (CN of free cyanoacetate), 122.4, 122.8, 126–129 (multiple lines from 3 phenyls of **6a** and **6b**), 130.2 (C^{tet} from phenyl of free cyanoacetate), 135.2, 136.4, 137.9, 140.2 (3 C^{tet} from phenyls and CN of **6a**), 137.1, 137.3, 138.3, 139.2 (3 C^{tet} from phenyls and CN of **6b**), 163.6 (CO of free cyanoacetate), 169.0 (CO of **6a**), 171.9 (CO of **6b**). IR (KBr, rt) $\nu_{\text{CN}} = 2174\text{ cm}^{-1}$.

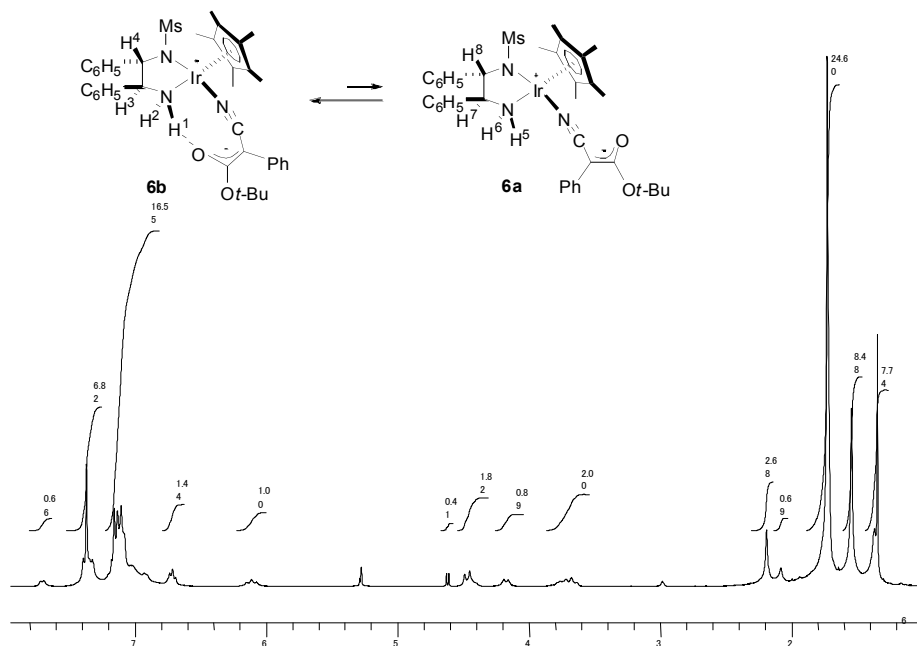


Figure S1. ^1H NMR spectrum of the equilibrium mixture of **6a** and **6b** (300 MHz, CD_2Cl_2 , 223K).

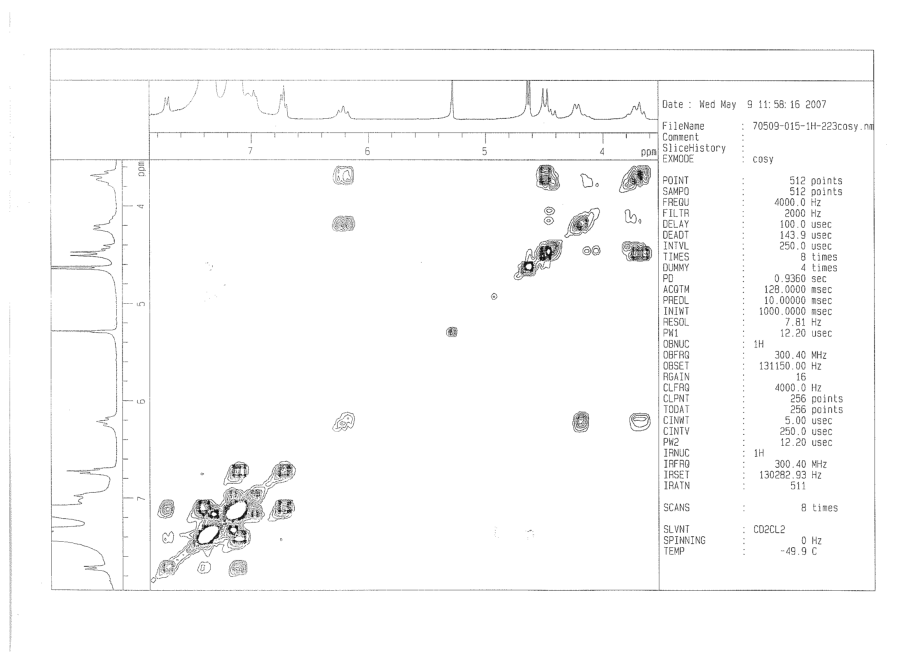


Figure S2. ^1H - ^1H COSY NMR spectrum of the equilibrium mixture of **6a** and **6b** (300 MHz, CD_2Cl_2 , 223 K).

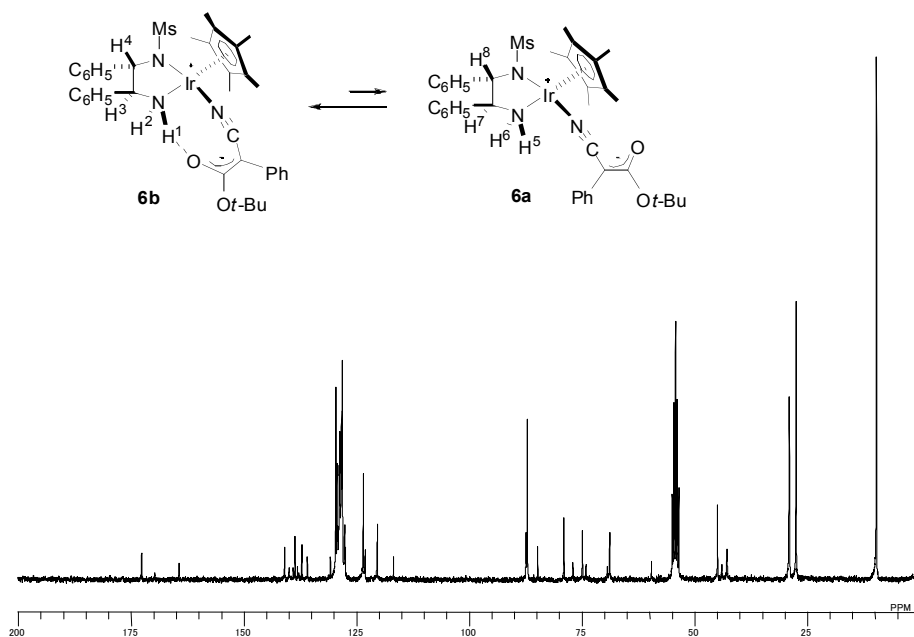


Figure S3. ^{13}C NMR spectrum of the equilibrium mixture of **6a** and **6b** (300 MHz, CD_2Cl_2 , 223K).

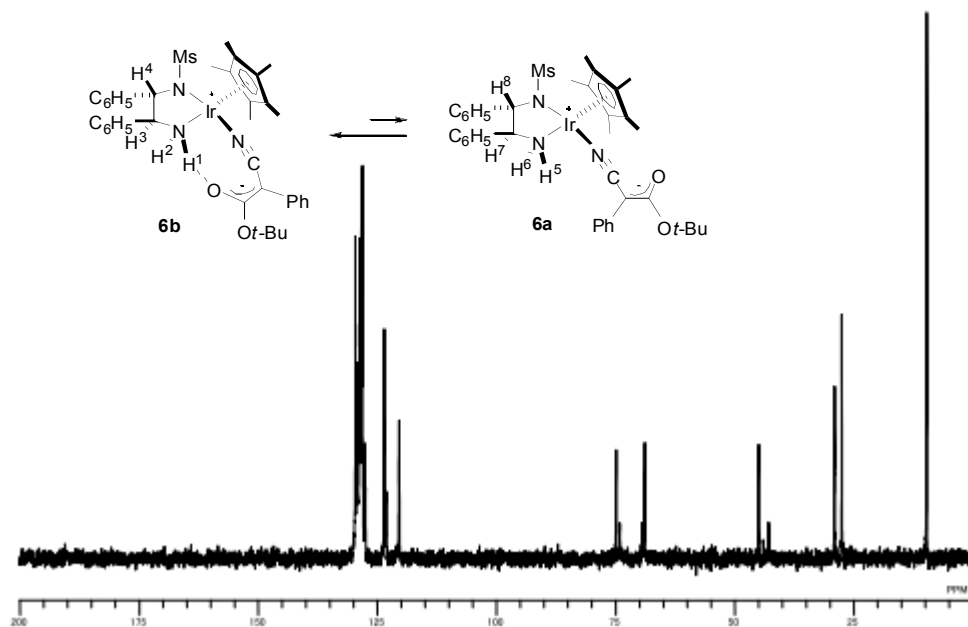


Figure S4. ^{13}C DEPT-135 NMR spectrum of the equilibrium mixture of **6a** and **6b**



Figure S5. Reversible line shape changes in the ^1H NMR spectrum due to the interconversion of **6a** and **6b** (300 MHz, CD_2Cl_2).

6) Computational details.

Geometries of all stationary points were optimized using analytical energy gradients of self-consistent-field^{S1} and density functional theory (DFT).^{S2} The latter utilized Becke's three-parameter exchange-correlation functional^{S3} including the nonlocal gradient corrections described by Lee-Yang-Parr (LYP),^{S4} as implemented in the Gaussian 03 program package.^{S5} All geometry optimizations were performed using the SDD basis set.^{S6} This approach is widely used for the recent computational studies of transition metal complexes, and was shown to yield results conforming with experimental data in the works of our own^{S7} and the others.^{S8}

(S1) Pulay, P. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 4, p. 153.

(S2) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989; (b) Cheeseman, J. R.; Frisch, M. J.; Devlin, F. J.; Stephens P. J. *Chem. Phys. Lett.* **1996**, 252, 211.

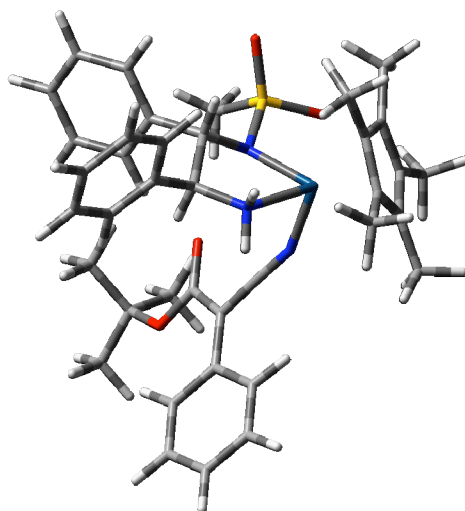
(S3) (a) Becke, A. D. *Phys. Rev. A* **1988**, 38, 3098; Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.

(S4) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B*, **1988**, 37, 785; (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, 157, 200.

(S5) Gaussian 03, Revision B.05, M. J. Frisch, *et al.* Gaussian, Inc., Pittsburgh PA, 2003.

(S6) (a) Dunning Jr., T. H.; Hay, P. J. in: "*Modern Theoretical Chemistry*", Ed. H. F. Schaefer, III (Plenum, New York, 1976), vol. 3, 1; (b) Leininger, T; Nicklass, A.; Stoll, H.; Dolg, M.; Schwerdtfeger, P. *J. Chem. Phys.* 105, 1052 (1996).

- (S7) (a) Nakamura, I.; Bajracharya, G. B.; Wu, H.; Oishi, K.; Mizushima, Y.; Gridnev, I. D.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 15423; (b) Nakamura, I.; Mizushima, Y.; Gridnev, I. D.; Yamamoto, Y. *J. Am. Chem. Soc.* **2005**, *127*, 9844; (c) Nishikata, T.; Yamamoto, Y.; Gridnev, I. D.; Miyaura, N. *Organometallics* **2005**, *25*, 5025; (d) Gridnev, I. D.; del Rosario, M. K. C.; Zhanpeisov, N. U. *J. Phys. Chem. B.* **2005**, *109*, 12498; (e) Patil, N. T.; Lutete, L. M.; Wu, H.; Pahadi, N.; Gridnev, I. D.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 4270.
- (S8) (a) Bittner, M.; Koppel, H. *J. Phys. Chem. A.* 2004; *108*, 11116; (b) McKee, M. L.; Swart, M. *Inorg. Chem.* **2005**, *44*, 6975; (c) Kondo, T.; Tsunawaki, F.; Ura, Y.; Sadaoka, K.; Iwasa, T.; Wada, K.; Mitsudo, T. *Organometallics* **2005**, *24*, 905; (d) Nowroozi-Isfahani, T.; Musaev, D. G.; McDonald, F. E.; Morokuma, K. *Organometallics* **2005**, *24*, 2921.



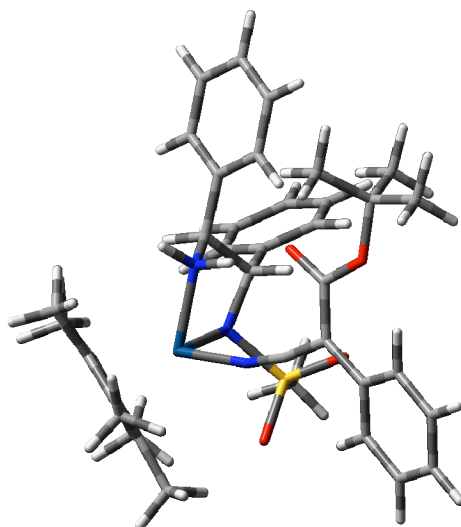
6a -2443.05255687 A.U.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	1.165325	0.062356	1.676766
2	1	0	0.558260	-0.564569	2.215296
3	1	0	1.994546	0.257642	2.244083
4	6	0	0.890484	1.938252	0.039449
5	1	0	1.920304	2.323346	0.125899
6	6	0	0.419162	1.364630	1.406997
7	1	0	-0.628505	1.079723	1.286368
8	6	0	4.025911	-0.965564	0.070498
9	6	0	3.478342	-2.111742	0.824735
10	6	0	3.742446	-1.195075	-1.336632
11	6	0	2.810091	-2.983750	-0.108889
12	6	0	2.935959	-2.397184	-1.454491
13	6	0	3.674053	-2.358047	2.297486
14	1	0	4.619254	-2.891457	2.472611
15	1	0	3.727807	-1.422400	2.868391
16	1	0	2.868364	-2.967998	2.720237
17	6	0	4.946164	0.098758	0.608927
18	1	0	5.993673	-0.237062	0.579498
19	1	0	4.877885	1.015919	0.014036
20	1	0	4.719825	0.352262	1.652501
21	6	0	4.304281	-0.375444	-2.463186
22	1	0	5.389603	-0.553575	-2.520774
23	1	0	3.843479	-0.639234	-3.414681

24	1	0	4.141804	0.699339	-2.324698
25	6	0	2.479971	-3.039654	-2.734463
26	1	0	3.306159	-3.593997	-3.205202
27	1	0	1.661692	-3.744591	-2.554395
28	1	0	2.119111	-2.276601	-3.428451
29	6	0	2.138951	-4.293439	0.199129
30	1	0	2.789273	-5.132168	-0.087809
31	1	0	1.912056	-4.394010	1.265640
32	1	0	1.199789	-4.394662	-0.353774
33	6	0	-2.699962	-1.539273	0.157134
34	7	0	0.826360	0.753040	-0.872503
35	16	0	1.114101	1.149663	-2.599294
36	8	0	2.216944	2.352519	-2.770868
37	8	0	1.437152	-0.252397	-3.362012
38	6	0	-0.542838	1.684388	-3.337105
39	1	0	-1.284922	1.002408	-2.915092
40	1	0	-0.708672	2.722605	-3.059394
41	1	0	-0.401658	1.551828	-4.411363
42	6	0	0.565931	2.312362	2.588840
43	6	0	-0.548269	2.609251	3.400477
44	6	0	1.818977	2.881426	2.915840
45	6	0	-0.418272	3.456724	4.516438
46	1	0	-1.519797	2.185516	3.154349
47	6	0	1.953013	3.724958	4.032018
48	1	0	2.689540	2.688702	2.289895
49	6	0	0.833473	4.015294	4.837093
50	1	0	-1.287843	3.680381	5.129183
51	1	0	2.920389	4.161511	4.268504
52	1	0	0.935216	4.671239	5.698100
53	6	0	-0.024416	3.105749	-0.336064
54	6	0	0.517520	4.393461	-0.517923
55	6	0	-1.420160	2.923654	-0.463694
56	6	0	-0.318126	5.490214	-0.800099
57	1	0	1.594146	4.533324	-0.459667
58	6	0	-2.256759	4.017243	-0.743819
59	1	0	-1.845868	1.925146	-0.398080
60	6	0	-1.710174	5.306527	-0.906387
61	1	0	0.114391	6.477444	-0.943568
62	1	0	-3.328154	3.862251	-0.845652
63	1	0	-2.358565	6.152308	-1.123701
64	6	0	-1.320631	-1.599652	-0.037657
65	7	0	-0.142303	-1.684192	-0.177751
66	6	0	-3.387474	-0.765163	-0.863463
67	8	0	-2.801910	-0.108416	-1.777822
68	8	0	-4.777631	-0.785274	-0.762004
69	6	0	-3.266354	-2.248934	1.332334

70	6	0	-4.605900	-2.085769	1.782543
71	6	0	-2.435990	-3.125622	2.091076
72	6	0	-5.075431	-2.755249	2.925775
73	1	0	-5.270211	-1.441792	1.223475
74	6	0	-2.909751	-3.790655	3.233025
75	1	0	-1.412104	-3.305093	1.768244
76	6	0	-4.237806	-3.611297	3.666572
77	1	0	-6.107410	-2.605067	3.238570
78	1	0	-2.244548	-4.457991	3.778618
79	1	0	-4.609395	-4.127449	4.548586
80	77	0	1.788751	-0.965873	-0.099258
81	6	0	-5.666355	-0.123100	-1.783097
82	6	0	-5.426607	1.400392	-1.785808
83	1	0	-4.433863	1.635988	-2.175534
84	1	0	-6.183491	1.889134	-2.413886
85	1	0	-5.516987	1.798969	-0.767155
86	6	0	-7.072234	-0.457167	-1.254543
87	1	0	-7.225248	-0.022845	-0.259279
88	1	0	-7.834919	-0.053356	-1.932505
89	1	0	-7.205208	-1.542393	-1.182241
90	6	0	-5.431535	-0.758630	-3.167484
91	1	0	-4.421244	-0.550090	-3.526825
92	1	0	-5.571409	-1.845169	-3.114159
93	1	0	-6.156246	-0.352905	-3.886060



6b -2443.06965536

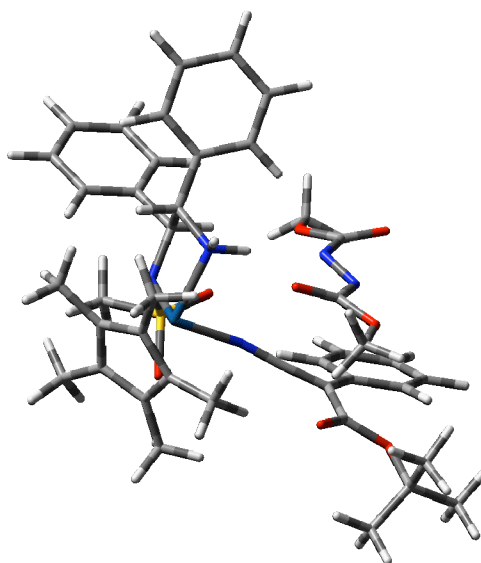
A.U.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	0.586188	0.624662	-1.398786
2	1	0	0.691852	0.711904	-2.413400
3	1	0	-0.414267	0.825847	-1.174010
4	6	0	1.379737	1.261423	0.818628
5	1	0	0.339900	1.456319	1.121156
6	6	0	1.513886	1.590334	-0.696428
7	1	0	2.530173	1.316126	-1.001289
8	6	0	0.969288	-3.171312	-2.105637
9	6	0	1.910792	-2.227404	-2.654296
10	6	0	1.470385	-3.586707	-0.779686
11	6	0	2.992208	-2.020670	-1.678950
12	6	0	2.727072	-2.909868	-0.547466
13	6	0	1.836797	-1.583867	-4.012488
14	1	0	2.381370	-2.191212	-4.749531
15	1	0	0.804104	-1.489145	-4.364502
16	1	0	2.295372	-0.587747	-4.017816
17	6	0	-0.267550	-3.710343	-2.771124
18	1	0	-0.077839	-4.708303	-3.192147
19	1	0	-1.094130	-3.801845	-2.058946
20	1	0	-0.605801	-3.062155	-3.586356
21	6	0	0.840653	-4.616095	0.118026
22	1	0	1.381146	-5.571720	0.050226
23	1	0	0.850860	-4.272333	1.156860

24	1	0	-0.201981	-4.800174	-0.159533
25	6	0	3.623769	-3.098713	0.641333
26	1	0	4.413267	-3.827517	0.404931
27	1	0	4.107259	-2.157320	0.925076
28	1	0	3.057025	-3.458771	1.503365
29	6	0	4.263503	-1.248069	-1.910363
30	1	0	5.023822	-1.874650	-2.400058
31	1	0	4.099289	-0.373643	-2.551475
32	1	0	4.687776	-0.893762	-0.964742
33	6	0	-3.261324	-0.510523	0.212269
34	7	0	1.708687	-0.214647	0.926148
35	16	0	1.027479	-0.839149	2.552577
36	8	0	-0.264659	0.009067	3.075851
37	8	0	0.918346	-2.463830	2.453754
38	6	0	2.404008	-0.533944	3.813459
39	1	0	3.293595	-1.030739	3.428397
40	1	0	2.532970	0.542710	3.905735
41	1	0	2.038592	-0.992193	4.734124
42	6	0	1.274833	3.047982	-1.070538
43	6	0	2.379554	3.859191	-1.408112
44	6	0	-0.021015	3.611239	-1.084403
45	6	0	2.202680	5.213404	-1.744544
46	1	0	3.382368	3.435891	-1.396096
47	6	0	-0.197066	4.964684	-1.425560
48	1	0	-0.888989	3.000172	-0.850717
49	6	0	0.909994	5.771216	-1.753857
50	1	0	3.064429	5.826944	-1.996380
51	1	0	-1.198548	5.388479	-1.435673
52	1	0	0.767233	6.817231	-2.014997
53	6	0	2.314488	2.117986	1.665176
54	6	0	1.790453	3.087106	2.544082
55	6	0	3.715769	1.965556	1.573203
56	6	0	2.649297	3.899237	3.310175
57	1	0	0.712657	3.198364	2.634887
58	6	0	4.576417	2.774953	2.333647
59	1	0	4.124863	1.193947	0.925015
60	6	0	4.045131	3.748217	3.205287
61	1	0	2.230856	4.641693	3.985363
62	1	0	5.653961	2.648192	2.254110
63	1	0	4.709421	4.374526	3.796200
64	6	0	-1.964209	-1.025970	0.136519
65	7	0	-0.834676	-1.305039	-0.060629
66	6	0	-3.304809	0.778919	-0.420943
67	8	0	-2.270381	1.361355	-0.927189
68	8	0	-4.556796	1.372281	-0.460281
69	6	0	-4.325263	-1.277004	0.895871

70	6	0	-5.710737	-1.002601	0.751244
71	6	0	-3.956488	-2.369067	1.731562
72	6	0	-6.674295	-1.787917	1.408901
73	1	0	-6.020227	-0.173782	0.128585
74	6	0	-4.922583	-3.152801	2.380551
75	1	0	-2.902525	-2.587688	1.893557
76	6	0	-6.294709	-2.870494	2.225313
77	1	0	-7.729246	-1.551822	1.278830
78	1	0	-4.603504	-3.975350	3.017790
79	1	0	-7.045126	-3.473593	2.731434
80	77	0	1.079142	-1.358794	-0.728646
81	6	0	-4.799824	2.768619	-0.964483
82	6	0	-4.046232	3.774851	-0.073320
83	1	0	-2.965402	3.655604	-0.173888
84	1	0	-4.320006	4.799567	-0.358227
85	1	0	-4.317394	3.624988	0.978415
86	6	0	-6.321500	2.914060	-0.786856
87	1	0	-6.599924	2.768114	0.262779
88	1	0	-6.644770	3.914553	-1.101469
89	1	0	-6.851549	2.169027	-1.391460
90	6	0	-4.406582	2.875046	-2.451118
91	1	0	-3.328497	2.756966	-2.578549
92	1	0	-4.917172	2.097725	-3.032953
93	1	0	-4.713518	3.854347	-2.842766



Associate of **6a** and **4a** capable to undergo enantioselective addition -
3009.35431892 A.U.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-1.280663	-0.346341	1.450988
2	1	0	-1.163157	-0.801959	2.359734
3	1	0	-0.611671	0.448770	1.452700
4	6	0	-2.724550	0.673821	-0.226638
5	1	0	-2.076065	1.560341	-0.239300
6	6	0	-2.702627	0.091555	1.220636
7	1	0	-3.309930	-0.820692	1.214148
8	6	0	0.463090	-3.550271	0.340571
9	6	0	-0.808947	-3.622861	1.019451
10	6	0	0.189729	-3.484869	-1.110057
11	6	0	-1.880476	-3.581291	0.019079
12	6	0	-1.238778	-3.548657	-1.300665
13	6	0	-1.004233	-3.738999	2.506903
14	1	0	-0.955329	-4.793467	2.813967
15	1	0	-0.229035	-3.196862	3.058472
16	1	0	-1.981864	-3.355399	2.820621
17	6	0	1.825450	-3.642290	0.969932
18	1	0	2.261178	-4.634862	0.779477
19	1	0	2.517284	-2.887284	0.582620

20	1	0	1.768676	-3.502160	2.054326
21	6	0	1.230560	-3.445013	-2.194780
22	1	0	1.386709	-4.448250	-2.618253
23	1	0	0.925601	-2.768694	-2.999548
24	1	0	2.189977	-3.091667	-1.805037
25	6	0	-1.953844	-3.620898	-2.618519
26	1	0	-2.084883	-4.672196	-2.915688
27	1	0	-2.948424	-3.166100	-2.555618
28	1	0	-1.392116	-3.102557	-3.399506
29	6	0	-3.348502	-3.797829	0.270100
30	1	0	-3.607893	-4.864636	0.199939
31	1	0	-3.646836	-3.454470	1.267544
32	1	0	-3.958143	-3.261257	-0.464968
33	6	0	3.152546	0.697912	-0.644712
34	7	0	-2.153588	-0.433352	-1.092112
35	16	0	-1.606701	0.277393	-2.710997
36	8	0	-1.209559	1.865676	-2.646788
37	8	0	-0.526986	-0.749253	-3.371516
38	6	0	-3.124028	0.189203	-3.834062
39	1	0	-3.441929	-0.852534	-3.846243
40	1	0	-3.879468	0.851006	-3.414818
41	1	0	-2.766334	0.525421	-4.808768
42	6	0	-4.134846	1.065563	-0.655133
43	6	0	-4.475459	2.422250	-0.827770
44	6	0	-5.127743	0.083417	-0.868384
45	6	0	-5.781626	2.795006	-1.199529
46	1	0	-3.717293	3.185519	-0.672741
47	6	0	-6.433328	0.449477	-1.236899
48	1	0	-4.864869	-0.966980	-0.768757
49	6	0	-6.766261	1.809762	-1.403678
50	1	0	-6.028069	3.846042	-1.329935
51	1	0	-7.187946	-0.317350	-1.398173
52	1	0	-7.775387	2.095255	-1.691361
53	6	0	1.897273	0.083497	-0.567172
54	7	0	0.835373	-0.410048	-0.421119
55	6	0	4.234465	-0.137547	-0.132646
56	8	0	4.051182	-1.266067	0.420662
57	8	0	5.494844	0.391597	-0.332655
58	6	0	3.259337	1.996490	-1.343289
59	6	0	4.364247	2.875242	-1.174415
60	6	0	2.201619	2.418573	-2.198100
61	6	0	4.410450	4.108260	-1.841476
62	1	0	5.171606	2.587158	-0.515488
63	6	0	2.256989	3.652010	-2.865386
64	1	0	1.332171	1.786780	-2.356356
65	6	0	3.362655	4.508074	-2.696343

66	1	0	5.264120	4.764933	-1.686283
67	1	0	1.436522	3.933489	-3.521659
68	1	0	3.407214	5.463548	-3.214411
69	77	0	-0.737559	-1.665417	-0.128607
70	6	0	6.761954	-0.363688	-0.020817
71	6	0	6.847786	-0.651100	1.490287
72	1	0	6.096650	-1.385816	1.786536
73	1	0	7.846284	-1.040108	1.731056
74	1	0	6.687123	0.271364	2.060981
75	6	0	7.846474	0.635962	-0.456685
76	1	0	7.783871	1.554928	0.137467
77	1	0	8.842069	0.195819	-0.317278
78	1	0	7.721338	0.898911	-1.512790
79	6	0	6.814670	-1.648469	-0.870426
80	1	0	6.020293	-2.340904	-0.580587
81	1	0	6.704276	-1.405421	-1.934160
82	1	0	7.785025	-2.142653	-0.728994
83	7	0	0.842708	1.952083	1.697081
84	7	0	2.073567	1.696858	2.025157
85	6	0	2.187910	0.407384	2.695643
86	8	0	1.284546	-0.435543	2.867140
87	8	0	3.466945	0.272496	3.132227
88	6	0	0.685212	3.261968	1.083816
89	8	0	1.328517	4.288213	1.327556
90	8	0	-0.393998	3.168105	0.244335
91	6	0	3.815593	-1.009503	3.772023
92	1	0	3.814219	-1.791277	3.008560
93	1	0	4.816618	-0.855775	4.175048
94	1	0	3.099358	-1.242433	4.566746
95	6	0	-0.684965	4.313946	-0.643609
96	1	0	-1.102481	3.855275	-1.541139
97	1	0	-1.398893	4.976087	-0.141379
98	1	0	0.238349	4.854356	-0.865712
99	6	0	-3.247782	1.016309	2.303988
100	6	0	-4.565360	0.821556	2.772430
101	6	0	-2.475494	2.059539	2.859693
102	6	0	-5.108751	1.657072	3.764749
103	1	0	-5.172346	0.020760	2.354328
104	6	0	-3.014782	2.892463	3.856470
105	1	0	-1.454603	2.216191	2.528846
106	6	0	-4.333433	2.697972	4.310990
107	1	0	-6.127143	1.495825	4.110171
108	1	0	-2.406001	3.688882	4.277830
109	1	0	-4.748041	3.343719	5.081417

M