Enantioselective Synthesis of 1,2,4-Triazolines by Chiral Iron(II)-Complex Catalyzed Cyclization of α-Isocyano Esters and Azodicarboxylates

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Supporting Information

A. General

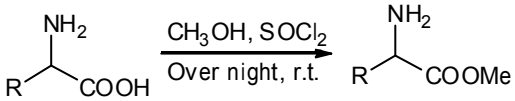
^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0). The enantiomeric excesses were determined by HPLC analysis on chiral DAICEL CHIRALCEL AD-H, IB, OD-H column. Optical rotations were measured on a commercial polarimeter and reported as follows: $[\alpha]^T_D$ (c = g/100 mL, solvent). DEAD and dibenzyl azodicarboxylate (DBAD) were used after a single purification by column chromatography on silica gel. The other reagents obtained from commercial sources were used without further purification. CH_2Cl_2 were distilled over CaH_2 before use. THF, toluene, Et_2O were distilled over metal sodium before use, the other solvents were used without further purification.

B. General procedure for the chiral ligands preparation

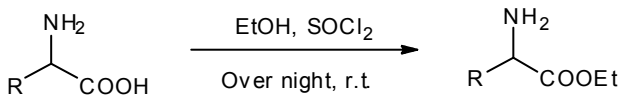
The *N,N*-dioxides were prepared according to the methods reported in the literature.[1]

C. General procedure for the synthesis of the α-isocyano esters

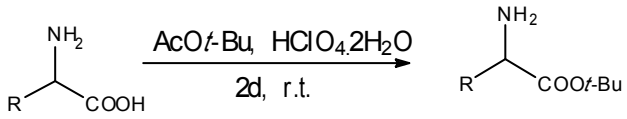
Isocyano esters **1** were synthesized according to literature procedures.[2]



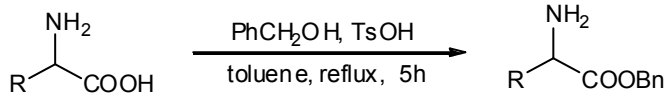
General procedure: To a solution of amino acid (10 mmol) in CH_3OH (20 mL) at room temperature was added dropwise $SOCl_2$ (2 mL). The reaction was stirred over night at room temperature, quenched with H_2O (20 mL) and then washed with K_2CO_3 (sat.) till no CO_2 released. The mixture was extracted with DCM, dried with Na_2SO_4 and concentrated in vacuum to give the corresponding product, which was used without any further purification.



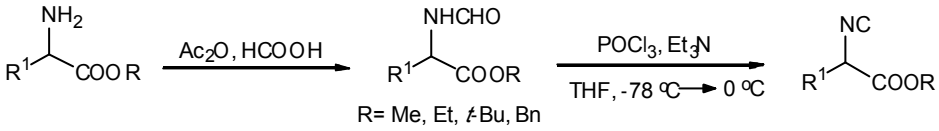
General procedure: To a solution of amino acid (10 mmol) in EtOH (20 mL) at room temperature was added dropwise $SOCl_2$ (2 mL). The reaction was stirred over night at room temperature, quenched with H_2O (20 mL) and then washed with K_2CO_3 (sat.) till no CO_2 released. The mixture was extracted with DCM, dried with Na_2SO_4 and concentrated in vacuum to give the corresponding product, which was used without further purification.



General procedure: To a solution of amino acid (10 mmol) in AcO*t*-Bu (40 mL) at room temperature was added dropwise $HClO_4{\cdot}2H_2O$ (2 mL). The reaction was stirred for 2 days at room temperature, and quenched with H_2O (20 mL) and then washed with K_2CO_3 (sat.) till no CO_2 released. The mixture was extracted with DCM, dried with Na_2SO_4 and concentrated in vacuum to give the corresponding product, which was used without further purification.

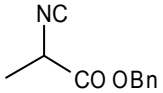


General procedure: To a solution of amino acids (10 mmol) in toluene (20 mL) was added $PhCH_2OH$ (4 mL) and TsOH (2.1 g, 12 mmol), then the mixture was heated to reflux for 5 hours. 15 mL Et_2O/petroleum ether (v/v = 1:1) was added when the reaction was cooled to room temperature. Until no precipitates precipitated, the mixture was filtered to provide the solid which was treated with NaOH (1N) till the pH > 7. The mixture was extracted with DCM, dried with Na_2SO_4 and concentrated in vacuum to give the corresponding product, which was used without further purification.

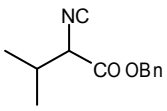


General procedure: To a solution of amino ester (17 mmol) in formic acid (32 mL) at 0 °C was added dropwise acetic anhydride (10.8 mL, 107 mmol). The reaction was stirred at rt for 5 hours, quenched with H_2O (40 mL) and then extracted with CH_2Cl_2 (5 x 70 mL). The combined organic layers were washed with $NaHCO_3$ (sat.) (5 x 70 mL), brine, dried (Na_2SO_4) and concentrated in vacuum to give the corresponding *N*-formamide ester.

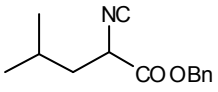
To a stirred solution of *N*-formamide ester (17 mmol) in dry THF (50 mL) at -78 °C under N_2 atmosphere was added Et_3N (12 mL, 85 mmol). A solution of $POCl_3$ (2 mL, 20 mmol) in dry THF (5 mL) was added dropwise and after that, the reaction mixture was allowed to warm to 0 °C. After stirring for another 2 hours, ice-cold water (60 mL) was added and the mixture was extracted with Et_2O (4 x 50 mL). The combined organic layers were washed with brine, dried with Na_2SO_4 and concentrated in vacuum. Purification by FC on silica gel afforded the corresponding isocyano ester **1**.



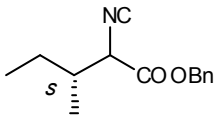
1d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (m, 5H), 5.22 (s, 2H), 4.36 (q, J = 7.1 Hz, 1H), 1.61 (t, J = 16.8 Hz, 3H) ppm.



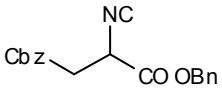
1e: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (m, 5H), 5.23 (s, 2H), 4.20 (d, J = 4.2 Hz, 1H), 1.08 (d, J = 6.8 Hz, 3H), 0.96 (d, J = 6.7 Hz, 3H) ppm.



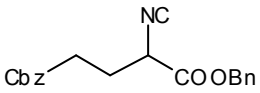
1f: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (m, 5H), 5.23 (s, 2H), 4.31 (dd, J = 9.7, 4.6 Hz, 1H), 3.71 (q, J = 7.0 Hz, 1H), 1.97 – 1.78 (m, 2H), 0.96 (t, J = 6.4 Hz, 6H) ppm.



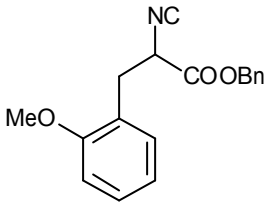
1g: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (m, 5H), 5.23 (d, J = 2.7 Hz, 2H), 4.35 (d, J = 3.6 Hz, 1H), 4.22 (d, J = 4.5 Hz, 1H), 2.07 (d, J = 4.0 Hz, 1H), 1.57 – 1.32 (m, 2H), 0.96 (ddd, J = 20.4, 16.4, 8.2 Hz, 6H) ppm.



1h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.27 (m, 10H), 5.26 – 5.09 (m, 4H), 4.70 (dd, J = 6.8, 5.8 Hz, 1H), 3.04 (qd, J = 16.9, 6.3 Hz, 2H) ppm.



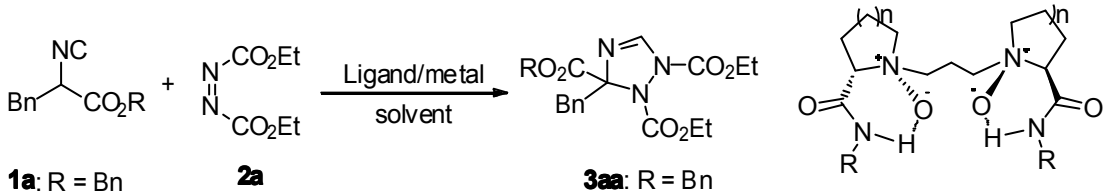
1i: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, J = 2.9 Hz, 10H), 5.23 (s, 2H), 5.13 (s, 2H), 4.49 (dd, J = 8.3, 4.9 Hz, 1H), 2.70 – 2.49 (m, 2H), 2.27 (dtd, J = 20.7, 14.1, 6.4 Hz, 2H) ppm.



1j: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.23 (m, 6H), 7.14 (dd, J = 7.4, 1.3 Hz, 1H), 6.89 (dd, J = 14.2, 7.7 Hz, 2H), 5.52 – 5.07 (m, 2H), 4.66 (dd, J = 8.8, 5.8 Hz, 1H), 3.82 (s, 3H), 3.37 (dd, J = 13.4, 5.7 Hz, 1H), 3.08 (dd, J = 13.4, 8.8 Hz, 1H) ppm.

D. Optimization of the reaction conditions

Table 1 The effects central metals on catalytic asymmetric addition of α-isocyano ester **1a** and DEAD.



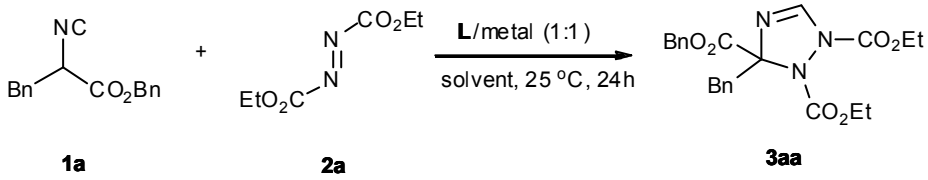
1a: R = Bn **2a** **3aa**: R = Bn **L1**: R = Ph, n = 2

Entry [a]	Ligand	Metal	Solvent	Yield (%) [b]	ee (%) [c]
1	**L1**	$Yb(OTf)_3$	THF	nr [d]	-
2	**L1**	$Sm(OTf)_3$	THF	nr [d]	-
3	**L1**	$Mg(OTf)_2$	THF	53	19
4	**L1**	$Zn(OTf)_2$	THF	nr [d]	-
5	**L1**	$Sc(OTf)_3$	THF	nr [d]	-
6	**L1**	$Cu(OTf)_2$	THF	91	2
7	**L1**	$Ni(acac)_2$	THF	66	21
8	**L1**	$Co(acac)_2$	THF	44	28

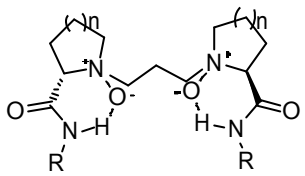
9	**L1**	$Fe(acac)_3$	THF	61	31
10	**L1**	$Fe(acac)_2$	THF	81	33
11	**L1**	$Fe(BF_4)_2\,6H_2O$	THF	nr [d]	-
12	**L1**	$Fe(OMe)_2$	THF	28	5
13	**L1**	$Fe(OAc)_2$	THF	68	28
14	**L1**	$Fe(ClO_4)_2\,6H_2O$	THF	nr [d]	-

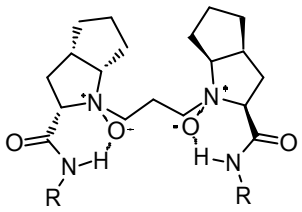
[a] Unless otherwise noted, all reactions were carried out with 10 mol% of **L1**/metal (1:1), **1a** (0.05 mmol), **2a** (0.075 mmol) in 0.5 mL THF at 25 °C for 24 h. [b] Isolated yield of **3aa**. [c] Determined by HPLC analysis using AD-H column. [d] No reaction.

Table 2 The effects of ligands on catalytic asymmetric addition of α-isocyano ester **1a** and DEAD.



1a **2a** **3aa**





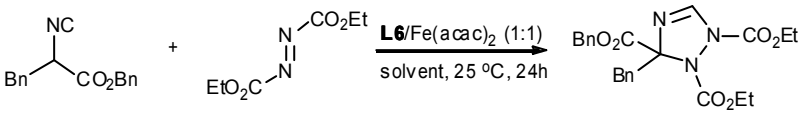
L1: R = phenyl, n=2
L2: R = phenyl, n=1
L3: R = 2,6-diisopropylphenyl, n=2
L4: R = (*S*)-phenylethyl, n=2
L5: R = diphenylmethyl, n=2
L6: R = 1-adamantanyl, n = 2
L8: R = 1-adamantanyl, n = 1

L7: R = phenyl
L9: R = 1-adamantanyl

Entry [a]	Ligand	Metal	solvent	Yield (%) [b]	ee (%) [c]
1	**L1**	$Fe(acac)_2$	THF	81	33
2	**L2**	$Fe(acac)_2$	THF	nd [e]	14
3	**L3**	$Fe(acac)_2$	THF	95	27
4	**L4**	$Fe(acac)_2$	THF	85	50
5	**L5**	$Fe(acac)_2$	THF	96	51
6	**L6**	$Fe(acac)_2$	THF	88	57
7	**L7**	$Fe(acac)_2$	THF	nr [d]	-
8	**L8**	$Fe(acac)_2$	THF	60	25
9	**L9**	$Fe(acac)_2$	THF	91	37

[a] Unless otherwise noted, all reactions were carried out with 10 mol% of **L**/$Fe(acac)_2$ (1:1), **1a** (0.05 mmol), **2a** (0.075 mmol) in 0.5 mL THF at 25 ℃ for 24 h. [b] Isolated yield of **3aa**. [c] Determined by HPLC analysis using AD-H column. [d] No reaction. [e] Not determined.

Table 3 The effects of solvents on catalytic asymmetric cyclization of α-isocyano ester **1a** and DEAD.

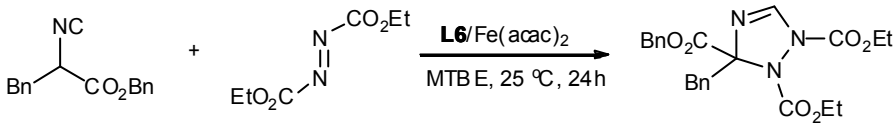


1a **2a** **3aa**

Entry [a]	Ligand	Metal	Solvent	Yield (%) [b]	ee (%) [c]
1	**L6**	$Fe(acac)_2$	THF	88	57
2	**L6**	$Fe(acac)_2$	CH_2Cl_2	96	13
3	**L6**	$Fe(acac)_2$	Et_2O	54	61
4	**L6**	$Fe(acac)_2$	toluene	89	39
5	**L6**	$Fe(acac)_2$	MTBE [d]	94	65
6	**L6**	$Fe(acac)_2$	*n*-Bu_2O	88	37
7	**L6**	$Fe(acac)_2$	*i*-Pr_2O	77	51

[a] Unless otherwise noted, all reactions were carried out with 10 mol% of **L6**/$Fe(acac)_2$ (1:1), **1a** (0.05 mmol), **2a** (0.075 mmol) in 0.5 mL solvent at 25 ℃ for 24 h. [b] Isolated yield of **3aa**. [c] Determined by HPLC analysis. [d] MTBE = methyl *tert*-butyl ester.

Table 4 The effects of the ligand/metal ratio on the catalytic asymmetric cyclization of α-isocyano ester **1a** and DEAD.

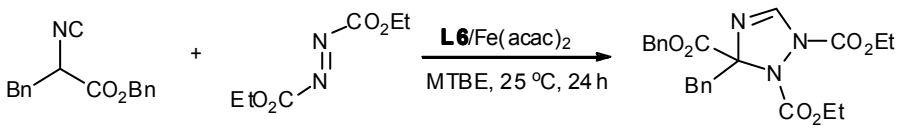


1a **2a** **3aa**

Entry [a]	Ligand	Metal	**L6**/$Fe(acac)_2$	Yield (%) [b]	ee % [c]
1	**L6**	$Fe(acac)_2$	1:1	94	65
2	**L6**	$Fe(acac)_2$	1.2:1	99	59
3	**L6**	$Fe(acac)_2$	1.5:1	99	61
4	**L6**	$Fe(acac)_2$	1:1.2	93	62
5	**L6**	$Fe(acac)_2$	1.5:1	95	65

[a] Unless otherwise noted, all reactions were carried out with 10 mol% of **L6**/$Fe(acac)_2$, **1a** (0.05 mmol), **2a** (0.075 mmol) in 0.5 mL MTBE at 25 ℃ for 24 h. [b] Isolated yield of **3aa**. [c] Determined by HPLC analysis.

Table 5 The effects of concentration on the catalytic asymmetric cyclization of α-isocyano ester **1a** and DEAD.



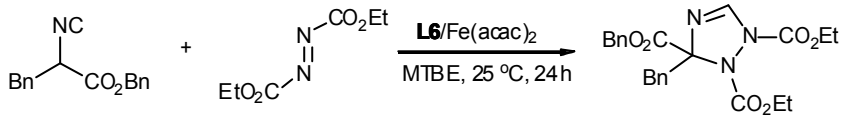
1a **2a** **3aa**

Entry [a]	Ligand	Metal	Amount of solvent	Yield (%) [b]	ee % [c]

1	**L6**	$Fe(acac)_2$	1.0 mL	70	73
2	**L6**	$Fe(acac)_2$	0.8 mL	91	69
3	**L6**	$Fe(acac)_2$	0.5 mL	94	65
4	**L6**	$Fe(acac)_2$	0.3 mL	95	65
5	**L6**	$Fe(acac)_2$	0.2 mL	99	58

[a] Unless otherwise noted, all reactions were carried out with 10 mol% of **L6**/$Fe(acac)_2$ (1:1), **1a** (0.05 mmol), **2a** (0.075 mmol) in MTBE at 25 °C for 24 h. [b] Isolated yield of **3aa**. [c] Determined by HPLC analysis.

Table 6 The effects of additives on catalytic asymmetric cyclization of α-isocyano ester **1a** and DEAD.

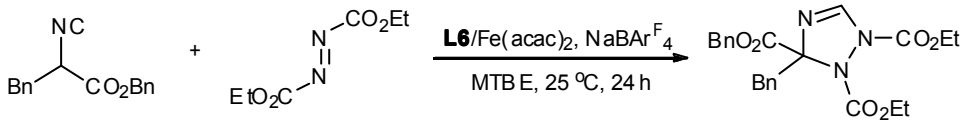


1a **2a** **3aa**

Entry [a]	Ligand	Metal	Additive	Yield (%) [b]	ee (%) [c]
1	**L6**	$Fe(acac)_2$	4Å MS(5.0 mg)	nd [d]	51
2	**L6**	$Fe(acac)_2$	$NaBAr^F{}_4$ [e]	99	88
3	**L6**	$Fe(acac)_2$	$CsCO_3$	33	53
4	**L6**	$Fe(acac)_2$	Na_2SO_4 (5.0 mg)	nd [d]	73
5	**L6**	$Fe(acac)_2$	$NaBAr^F{}_4$, DMAP	95	88
6	**L6**	$Fe(acac)_2$	$NaBAr^F{}_4$, DIPEA	97	87
7	**L6**	$Fe(acac)_2$	$NaBAr^F{}_4$, Diphenol	99	87
8	**L6**	$Fe(acac)_2$	$NaBAr^F{}_4$, H_2O	99	85
9	**L6**	$Fe(acac)_2$	$NaBAr^F{}_4$, $CaSO_4$	93	85

[a] Unless otherwise noted, all reactions were carried out with 10 mol% of **L6**/$Fe(acac)_2$ (1:1), additive (10 mol%), **1a** (0.05 mmol), **2a** (0.075 mmol) in 1.0 mL of MTBE at 25 °C for 24 h. [b] Isolated yield of **3aa**. [c] Determined by HPLC analysis. [d] Not determined. [e] $NaBAr^F{}_4$ = $NaB[3,5\text{-}(CF_3)_2C_6H_3]_4$.

Table 7 The effect of **1a**/**2a** ratio on catalytic asymmetric cyclization of α-isocyano ester **1a** and DEAD



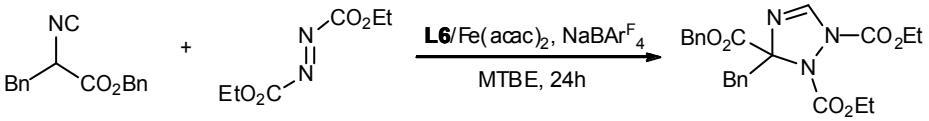
1a **2a** **3aa**

Entry [a]	**L**/Metal	**1a** (mmol)	**2a** (mmol)	Yield (%) [b]	ee (%) [c]
1	**L6**/$Fe(acac)_2$	0.05	0.05	84	88
2	**L6**/$Fe(acac)_2$	0.05	0.075	99	88
2	**L6**/$Fe(acac)_2$	0.05	0.10	99	85
3	**L6**/$Fe(acac)_2$	0.05	0.15	96	84
4	**L6**/$Fe(acac)_2$	0.075	0.05	92	87

5	**L6**/Fe(acac)$_2$	0.10	0.05	82	88
6	**L6**/Fe(acac)$_2$	0.15	0.05	96	87

[a] Unless otherwise noted, all reactions were carried out with 10 mol% of **L6**/Fe(acac)$_2$ (1:1), NaBAr$^F_4$ (10 mol%), **1a**, **2a** in 1.0 mL of MTBE at 25 °C for 24 h. [b] Isolated yield of **3aa**. [c] Determined by HPLC analysis.

Table 8 Effect of reaction temperature on catalytic asymmetric cyclization of α-isocyano ester **1a** and DEAD

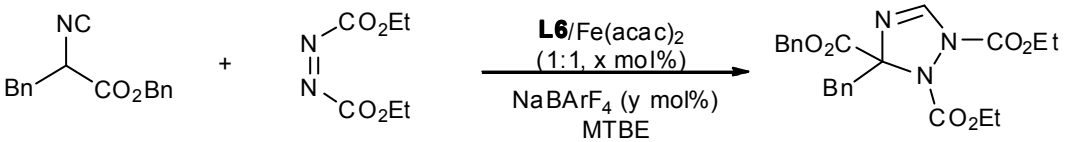


1a **2a** **3aa**

Entry [a]	**L**/Metal	Temperature (° C)	Yield (%) [b]	ee (%) [c]
1	**L6**/Fe(acac)$_2$	35	93	85
2	**L6**/Fe(acac)$_2$	30	91	87
3	**L6**/Fe(acac)$_2$	25	99	88
4	**L6**/Fe(acac)$_2$	0	39	79

[a] Unless otherwise noted, all reactions were carried out with **L6**/Fe(acac)$_2$ (1:1), NaBAr$^F_4$, **1a** (0.05 mmol), **2a** (0.075 mmol) in 1.0 mL of MTBE for 24 h. [b] Isolated yield of **3aa**. [c] Determined by HPLC analysis.

Table 9 The effect of catalyst and additive loading on catalytic asymmetric cyclization of α-isocyano ester **1a** and DEAD



1a **2a** **3aa**

Entry [a]	**L**/Metal	X (mol%)	Y (mol%)	Yield (%) [b]	ee (%) [c]
1	**L6**/Fe(acac)$_2$	15	15	96	85
2	**L6**/Fe(acac)$_2$	10	10	99	89
3	**L6**/Fe(acac)$_2$	5	5	99	89
4	**L6**/Fe(acac)$_2$	2.5	2.5	92	88
5	**L6**/Fe(acac)$_2$	5	10	99	89
6	**L6**/Fe(acac)$_2$	5	2.5	98	87
7 [d]	**L6**/Fe(acac)$_2$	5	5	97	89

[a] Unless otherwise noted, all reactions were carried out with **L6**/Fe(acac)$_2$ (1:1), NaBAr$^F_4$, **1a** (0.05 mmol), **2a** (0.075 mmol) in 1.0 mL of MTBE at 25 °C for 24 h. [b] Isolated yield of **3aa**. [c] Determined by HPLC analysis. [d] 0.1 mmol **1a**, 0.15 mmol **2a** and 2.0 mL of MTBE were used in the reaction.

E. General procedure for the asymmetric cyclization of α-isocyano esters and azodicarboxylates

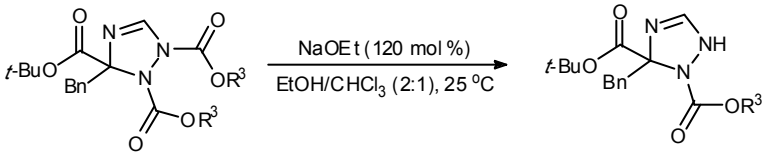
General procedure **A**: MTBE (2.0 mL) was added to a dry reaction tube containing a mixture of **L6** (3.0 mg, 0.005 mmol), $Fe(acac)_2$ (1.3 mg, 0.005 mmol), $NaBAr^F{}_4$ (4.4 mg, 0.005 mmol) and azodicarboxylate (0.15 mmol). The mixture was stirred at 25 °C for 1 hour, then isocyano ester **1** (0.1 mmol) was added. After being stirred for another 24 hours at 25 °C, the reaction mixture was directly purified by column chromatography on silica gel to afford the corresponding compound.

General procedure **B** for **3ea** and **3ga**: MTBE (1.0 mL) was added to a dry reaction tube containing a mixture of **L6** (3.0 mg, 0.005 mmol), $Fe(acac)_2$ (1.3 mg, 0.005 mmol), $NaBAr^F{}_4$ (4.4 mg, 0.005 mmol) and azodicarboxylate (0.075 mmol). The mixture was stirred at 25 °C for 1 h, then isocyano ester **1** (0.05 mmol) was added. After being stirred for 24 hours at 25 °C, the reaction mixture was directly purified by column chromatography on silica gel to afford the corresponding compound.

Typical procedure **C** for **3kb**, **3ab, 3ac** and **3ad**: MTBE (2.0 mL) was added to a dry reaction tube containing a mixture of **L6** (3.0 mg, 0.005 mmol), $Fe(acac)_2$ (1.3 mg, 0.005 mmol), $NaBAr^F{}_4$ (4.4 mg, 0.005 mmol) and azodicarboxylate (0.20 mmol). The mixture was stirred at 25 °C for 1 hour, then isocyano ester **1** (0.10 mmol) was added. After being stirred for 24 hours at 25 °C, the reaction mixture was directly purified by column chromatography on silica gel to afford the corresponding compound.

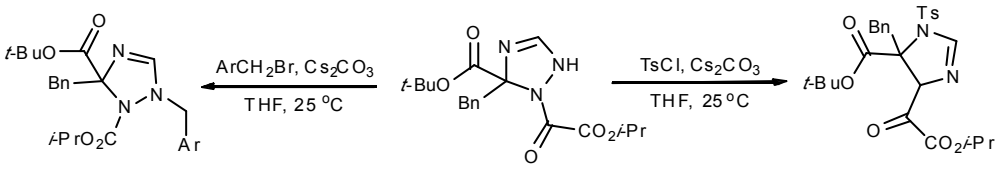
Typical procedure for gram-scale preparation: MTBE (60 mL) was added to a dry reaction flask containing a mixture of **L6** (90 mg, 1.5 mmol), $Fe(acac)_2$ (39 mg, 1.5 mmol), $NaBAr^F{}_4$ (132 mg, 1.5 mmol) and DIAD (6.0 mmol). The mixture was stirred at 25 °C for 1 hour, then isocyano ester **1k** (0.1 mmol) was added. After being stirred for 3d at 25 °C, the solvent was removed in vacuum, then the reaction mixture was purified by column chromatography on silica gel to afford the corresponding compound **3kb** in 71% yield with 93% ee.

F. Typical procedure for the mono-deprotection of the 1,2,4-triazoline (3ka, 3kb) and synthesis of 1,2,4-triazoline derivatives



R^3 = Et, **3ka**: 94% ee
R^3 = *i*-Pr. **3kb**: 93% ee

R^3 = Et, **4a**: 71 % yield, 94% ee
R^3 = *i*-Pr. **4b**: 73 % yield, 91% ee



Ar = 4-(4-ClC$_6$H$_5$COO)C$_6$H$_5$ Ts = 4-CH$_3$C$_6$H$_5$SO$_2$

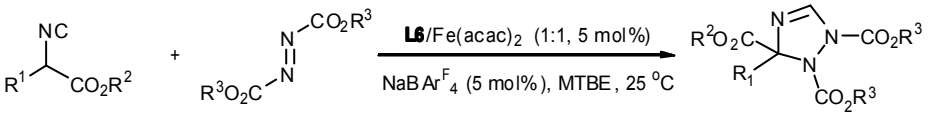
5a: 65 % yield, 91% ee **4b**: 91% ee **5b**: 95 % yield,91% ee

To a solution of **3** (0.035 mmol) in CH$_3$OH/EtOH (0.3 mL) (v/v = 1:2) was added NaOEt (3.0 mg, 0.042 mmol). Then the mixture was stirred for 3 days at 25 °C. The reaction was quenched with H$_2$O (1.0 ml), extracted with DCM (3 x 10 mL). The organic phase was dried with Na$_2$SO$_4$ and concentrated to give the crude product which was purified by column chromatography on silica gel to provide the corresponding compound **4**.

To a mixture of **4b** (10 mg, 0.029 mmol), 4-(bromomethyl)phenyl 4-chlorobenzoate (13.9 mg, 1.5 eq) and Cs$_2$CO$_3$ (12 mg, 1.2 eq) was added THF (1.0 mL), and the solution was stirred at 25 °C for 24 h, then was directly purified by column chromatography on silica gel to afford the corresponding compound **5a**.

To a mixture of **4b** (10 mg, 0.029 mmol), TsCl (11 mg, 2 eq) and Cs$_2$CO$_3$ (12 mg, 1.2 eq) was added THF (0.5 mL), and the solution was stirred at 25 ℃ for 36 h, then was directly purified by column chromatography on silica gel to afford the corresponding compound **5b**.

G. Substrate scope for the catalytic asymmetric cyclization of isocyano esters with azodicarboxylates [a]



1 **2** **3**

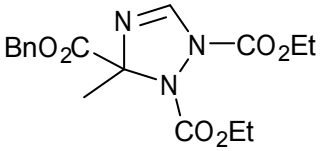
2a: R^3 = Et **2b**: R^3 = *i*-Pr
2c: R^3 = *t*-Bu **2d**: R^3 = Bn

Entry	R^1	R^2	**2**	Yield (%)[b]	ee (%)[c]
1	Me	Bn **(1d)**	**2a**	86 (**3da**)	82
2 [d]	*i*-Pr	Bn **(1e)**	**2a**	91 (**3ea**)	89
3	*i*-Bu	Bn **(1f)**	**2a**	91 (**3fa**)	88
4 [d]	(*S*)-sec-Bu	Bn **(1g)**	**2a**	83 (**3ga**)	80
5	CbzCH$_2$	Bn **(1h)**	**2a**	91 (**3ha**)	83
6	CbzCH$_2$CH$_2$	Bn **(1i)**	**2a**	98 (**3ia**)	83
7	*o*-MeOC$_6$H$_4$CH$_2$	Bn **(1j)**	**2a**	82 (**3ja**)	81
8	Bn	Me **(1b)**	**2a**	88 (**3ba**)	80
9	Bn	Et **(1c)**	**2a**	80 (**3ca**)	81
10	Bn	Bn **(1a)**	**2a**	97 (**3aa**)	89
11 [d]	Bn	*t*-Bu **(1k)**	**2a**	91 (**3ka**)	94
12 [e]	Bn	*t*-Bu **(1k)**	**2b**	86 (**3kb**)	93
13 [e]	Bn	Bn **(1a)**	**2b**	87 (**3ab**)	87
14 [e]	Bn	Bn **(1a)**	**2c**	72 (**3ac**)	81
15 [e]	Bn	Bn **(1a)**	**2d**	94 (**3ad**)	84

[a] Unless otherwise noted, all reactions were carried out with 5 mol% **L6**/Fe(acac)$_2$ (1:1), NaBAr$^F{}_4$ (5 mol%), **1** (0.1 mmol), **2** (0.15 mmol) in MTBE (2.0 mL) at 25 ºC for 24 h. [b] isolated yield. [c] Determined by HPLC analysis. [d] 10 mol% catalyst and additive were used in 1.0 mL of MTBE. [e] 0.2 mmol of **2** was used in the reaction.

H. The analytical and spectral characterization data of the reaction products

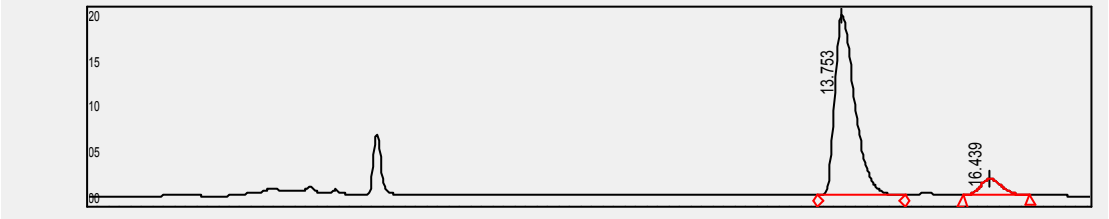
3-benzyl 1,2-diethyl 3-methyl-3H-1,2,4-triazole-1,2,3-tricarboxylate (3da)



Synthesized according to procedure **A**. The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 8:1 – 4:1) as yellow oil in 86% yield with 82% ee. $[\alpha]^{23}_D$ = 7.5 (c = 0.556, CH_2Cl_2); The ee value was determined by HPLC analysis using a chiralcel AD-H column. Eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (major) = 13.75 min, t_r (minor) = 16.43 min.

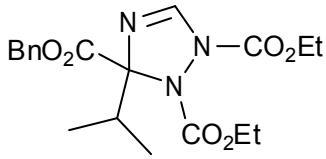
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.30 – 7.23 (m, 5H), 5.10 (s, 2H), 4.27 (dd, *J* = 14.4, 7.3 Hz, 2H), 4.00 (ddd, *J* = 14.3, 8.9, 5.3 Hz, 1H), 3.81 (dd, *J* = 10.3, 7.2 Hz, 1H), 1.74 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.56, 154.76, 150.65, 146.52, 134.82, 128.60, 128.51, 128.33, 93.46, 76.70, 68.00, 64.12, 62.93, 24.09, 14.25, 14.04 ppm; ES-HRMS Calcd for $C_{17}H_{21}N_3O_6$ [M + Na]$^+$ 386.1328, Found: 386.1324.

	Retention Time	% Area
1	13.788	50.01
2	16.386	49.99



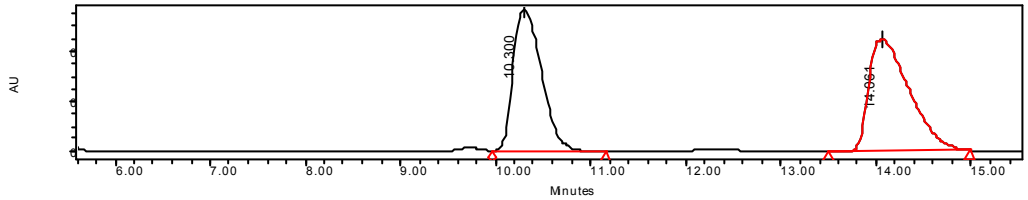
	Retention Time	% Area
1	13.753	90.96
2	16.439	9.04

3-benzyl 1,2-diethyl 3-isopropyl-3H-1,2,4-triazole-1,2,3-tricarboxylate (3ea)

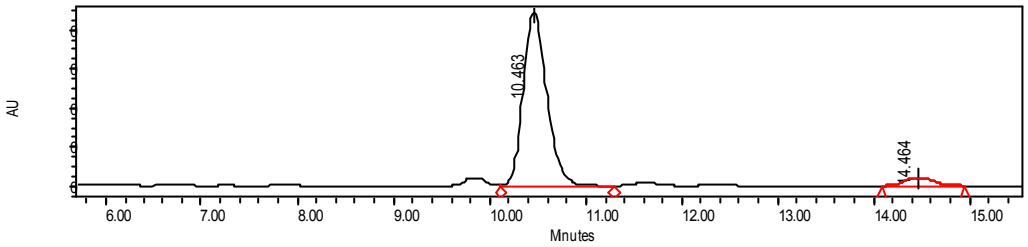


Synthesized according to procedure **B**. The crude product was purified by flash chromatography on silica gel (petroleum ether : ethyl acetate = 8 : 1 – 4 : 1) as yellow oil in 91% yield with 89% ee. $[\alpha]^{23}_{D}$ = 12.6 (c = 0.308, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel AD-H column. Eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (major) = 10.46 min, t_r (minor) = 14.46 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.36 – 7.24 (m, 5H), 5.08 (s, 2H), 4.37 – 4.20 (m, 2H), 3.97 (ddd, *J* = 14.3, 8.9, 5.3 Hz, 1H), 3.81 (dd, *J* = 10.3, 7.2 Hz, 1H), 2.54 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 4H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 155.45, 150.56, 146.08, 134.89, 128.56, 128.42, 128.29, 98.89, 67.71, 63.93, 62.95, 33.35, 16.98, 16.19, 14.30, 14.01 ppm; ES-HRMS Calcd for $C_{19}H_{25}N_3O_6$ $[M + Na]^+$ 414.1641, Found: 414.1640.

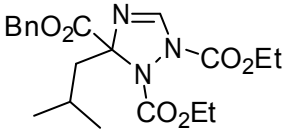


	Retention Time	% Area
1	10.300	46.83
2	14.061	53.17



	Retention Time	% Area
1	10.463	94.36
2	14.464	5.64

3-benzyl 1,2-diethyl 3-isobutyl-3H-1,2,4-triazole-1,2,3-tricarboxylate (3fa)

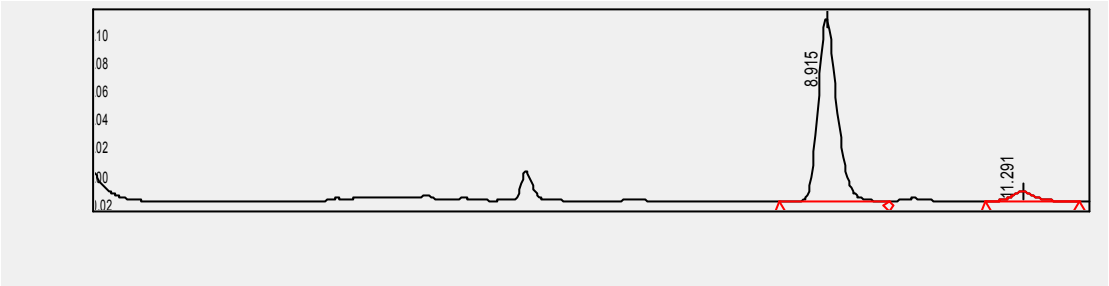


Prepared according to procedure **A**. The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 8:1 – 4:1) as yellow oil in 91% yield with 88% ee. $[\alpha]^{23}_{D}$ = 18.8 (c = 0.516, CH_2Cl_2); The ee value was determined by HPLC analysis using a chiralcel AD-H column. Eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (major) = 8.91 min, t_r (minor) = 11.29 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.36 – 7.24 (m, 5H), 5.08 (s, 2H), 4.37 – 4.20 (m, 2H),

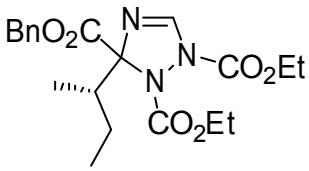
3.97 (ddd, J = 14.3, 8.9, 5.3 Hz, 1H), 3.81 (dd, J = 10.3, 7.2 Hz, 1H), 2.16 (dt, J = 13.5, 6.7 Hz, 1H), 2.06 (dt, J = 13.5, 6.7 Hz, 1H), 1.57 (m, 1H), 1.27 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.1 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H), 0.83 (d, J = 6.7 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 155.45, 150.56, 146.08, 134.89, 128.56, 128.42, 128.29, 98.89, 67.71, 63.93, 62.95, 33.35, 16.98, 16.19, 14.30, 14.01 ppm; ES-HRMS Calcd for $C_{20}H_{27}N_3O_6$ [M + Na]$^+$ 428.1798, Found: 428.1795.

	Retention Time	% Area
1	8.916	50.53
2	11.279	49.47



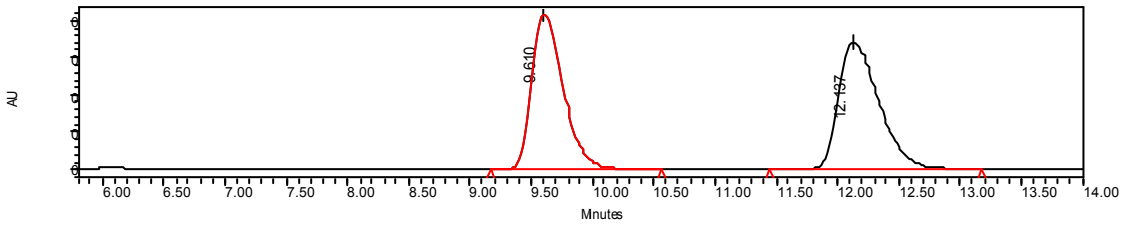
	Retention Time	% Area
1	8.915	93.93
2	11.291	6.07

3-benzyl 1,2-diethyl 3-sec-butyl-3H-1,2,4-triazole-1,2,3-tricarboxylate (3ga)

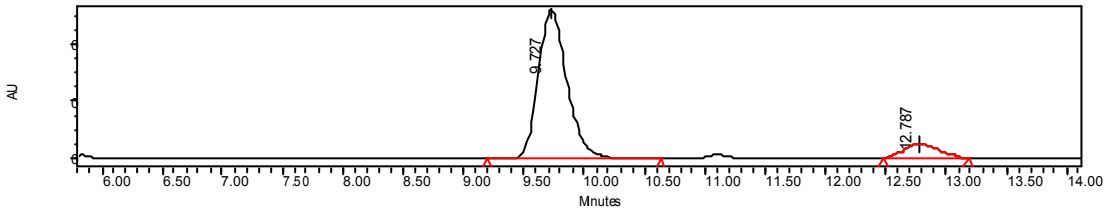


Prepared according to procedure **B**. The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 8:1 – 4:1) as yellow oil in 83% yield with 80% ee. $[\alpha]^{23}_D$ = 12.9 (c = 0.692, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel AD-H column. Eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (major) = 9.73 min, t_r (minor) = 12.79 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.35 – 7.23 (m, 5H), 5.17 – 5.03 (m, 2H), 4.33 – 4.20 (m, 2H), 4.03 – 3.93 (m, 1H), 3.87 – 3.73 (m, 1H), 2.14 (dd, J = 14.9, 5.7 Hz, 1H), 2.03 (dd, J = 14.9, 5.8 Hz, 1H), 1.60 – 1.51 (m, 1H), 1.28 (dd, J = 14.8, 7.6 Hz, 3H), 1.05 (t, J = 7.1 Hz, 3H), 0.86 (dd, J = 15.3, 6.7 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.74, 154.89, 150.75, 146.77, 134.88, 128.58, 128.47, 128.36, 96.24, 67.91, 64.03, 62.8, 43.12, 24.19, 23.95, 23.29, 14.23, 14.06 ppm; ES-HRMS Calcd for $C_{20}H_{27}N_3O_6$ [M + H]$^+$ 406.1978, Found: 406.1985.

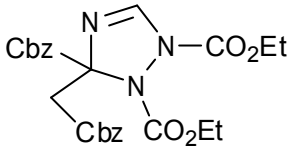


	Retention Time	% Area
1	9.610	48.97
2	12.137	51.03



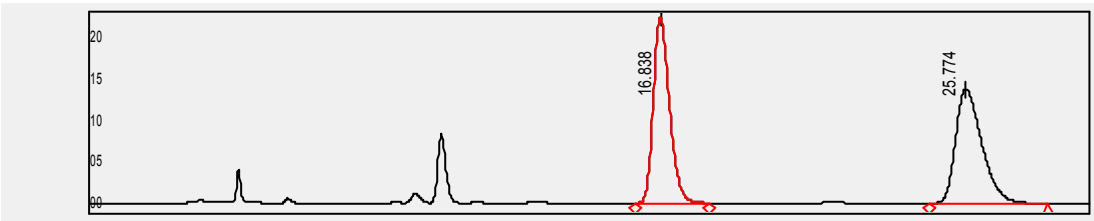
	Retention Time	% Area
1	9.727	89.82
2	12.787	10.18

3-benzyl 1,2-diethyl 3-(2-(benzyloxy)-2-oxoethyl)-3H-1,2,4-triazole-1,2,3-tricarboxylate (3ha)



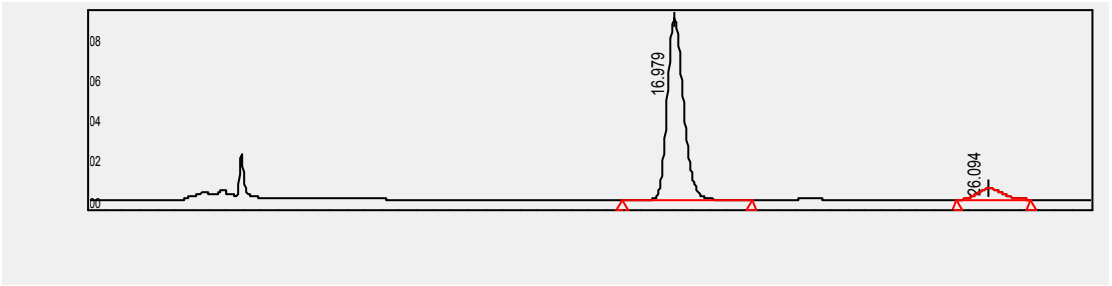
Prepared according to procedure **A**. The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 3:1) as yellow oil in 91% yield with 83% ee. $[\alpha]^{23}_{D}$ = 15.0 (c = 0.602, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel AD-H column. Eluent: Hexane/Isopropanol = 80/20; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (major) = 16.98 min, t_r (minor) = 26.09 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.33 – 7.21 (m, 10H), 5.16 – 5.05 (m, 2H), 5.03 – 4.94 (m, 2H), 4.23 (q, J = 7.0 Hz, 2H), 3.97 (ddd, J = 14.3, 8.8, 5.3 Hz, 1H), 3.82 (s, 1H), 3.38 (d, J = 17.6 Hz, 1H), 3.27 (d, J = 17.6 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.32, 166.54, 149.18, 135.47, 134.51, 128.64, 128.54, 128.43, 128.27, 128.20, 92.16, 68.33, 66.39, 63.80, 63.06, 39.45, 14.23, 14.06 ppm; ES-HRMS Calcd for $C_{25}H_{27}N_3O_8$ $[M + Na]^+$ 520.1696, Found: 520.1697.



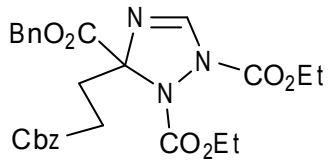
	Retention Time	% Area
1	16.838	50.14

2	25.774	49.86



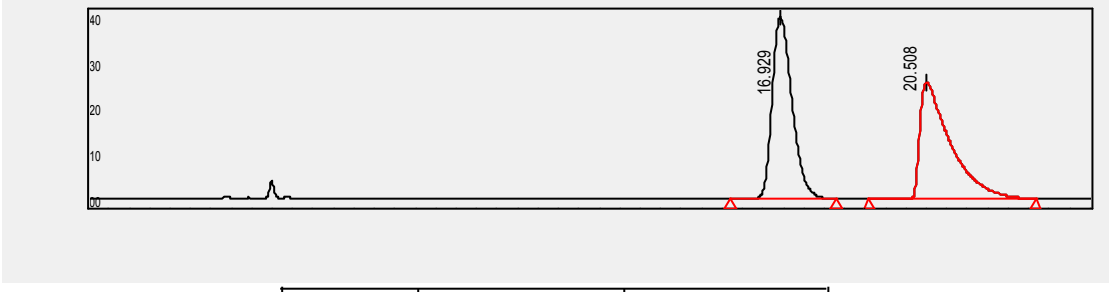
	Retention Time	% Area
1	16.979	91.50
2	26.094	8.50

3-benzyl 1,2-diethyl 3-(3-(benzyloxy)-3-oxopropyl)-3H-1,2,4-triazole-1,2,3-tricarboxylate (3ia)

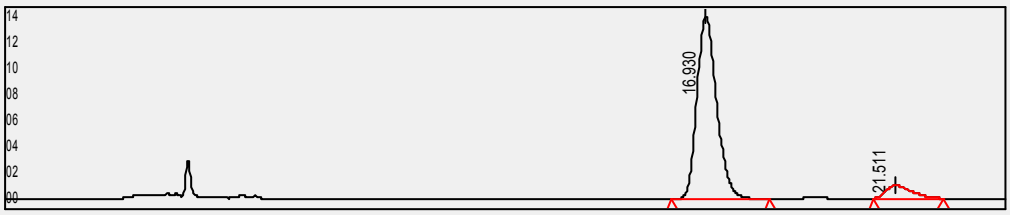


Prepared according to procedure **A**. The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate =3:1) as yellow oil in 98% yield with 83% ee. $[\alpha]^{23}_{D}$ = 12.4 (c = 0.618, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel AD-H column. Eluent: Hexane/Isopropanol = 80/20; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (major) = 16.93 min, t_r (minor) = 21.51 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.39 – 7.20 (m, 10H), 5.12 – 4.97 (m, 4H), 4.29 – 4.20 (m, 2H), 3.95 (dq, J = 10.6, 7.1 Hz, 1H), 3.78 (s, 1H), 2.59 – 2.42 (m, 2H), 2.42 – 2.24 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H), 1.03 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.41, 166.96, 150.31, 147.34, 135.84, 134.65, 128.62, 128.58, 128.54, 128.41, 128.34, 128.24, 95.23, 68.12, 66.46, 64.24, 63.12, 30.79, 28.28, 14.24, 13.99 ppm; ES-HRMS Calcd for $C_{26}H_{29}N_3O_8$ [M + Na]$^+$ 534.1852, Found: 534.1857.

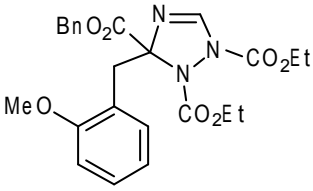


	Retention Time	% Area
1	16.929	50.08
2	20.508	49.92



	Retention Time	% Area
1	16.930	91.59
2	21.511	8.41

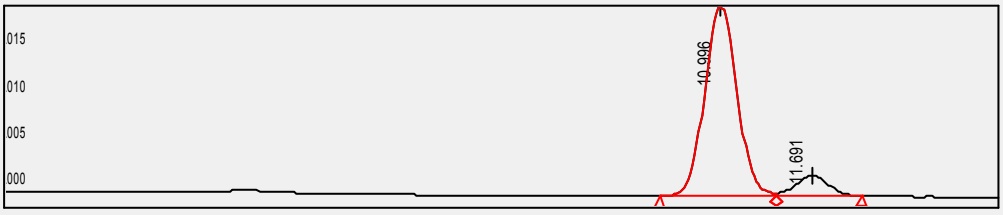
3-benzyl 1,2-diethyl 3-(2-methoxybenzyl)-3H-1,2,4-triazole-1,2,3-tricarboxylate (3ja)



Prepared according to procedure **A**. The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 3:1) as yellow oil in 82% yield with 81% ee. $[\alpha]^{23}_{D}$ = 7.3 (c = 0.670, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IA column. Eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (major) = 10.99 min, t_r (minor) = 11.69 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.29 (d, *J* = 3.7 Hz, 5H), 7.06 (dd, *J* = 15.6, 7.7 Hz, 2H), 6.70 (dd, *J* = 16.9, 8.0 Hz, 2H), 5.14 (s, 2H), 4.03 – 3.88 (m, 3H), 3.80 (d, *J* = 9.6 Hz, 1H), 3.70 (s, 3H), 3.63 – 3.58 (m, 1H), 3.40 (d, *J* = 14.0 Hz, 1H), 1.09 (dd, *J* = 16.2, 7.3 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.37, 158.73, 147.04, 134.90, 132.38, 128.59, 128.46, 128.36, 128.14, 122.09, 119.40, 110.62, 95.36, 67.97, 63.47, 62.67, 55.2, 34.08, 14.21, 14.16 ppm; ES-HRMS Calcd for $C_{24}H_{27}N_3O_7$ $[M + Na]^+$ 492.1747, Found: 492.1750.

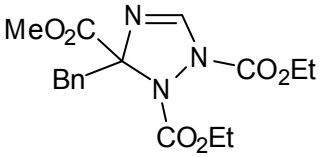
	Retention Time	% Area
1	10.898	49.08
2	11.563	50.92



	Retention Time	% Area
1	10.996	90.68

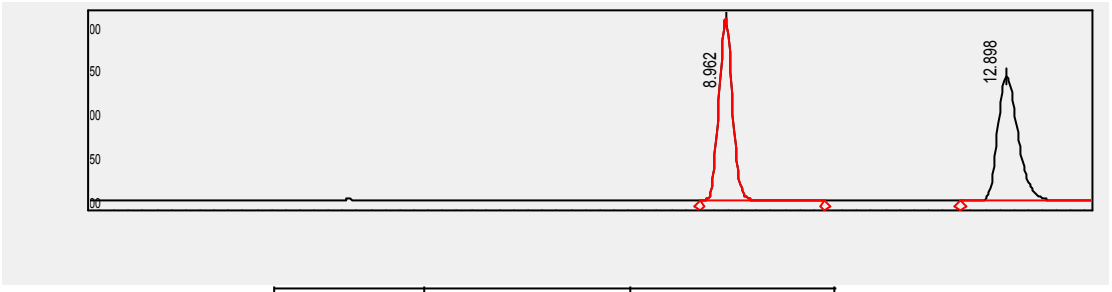
2	11.691	9.32

1,2-diethyl 3-methyl 3-benzyl-3H-1,2,4-triazole-1,2,3-tricarboxylate (3ba)



Prepared according to procedure **A**. The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 8:1 – 4:1) as yellow oil in 88% yield with 80% ee. $[\alpha]^{23}_{D}$ = 5.5 (c = 0.698, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel AD-H column. Eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (major) = 8.79 min, t_r (minor) = 12.71 min.

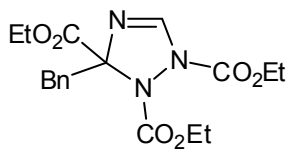
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.17 – 7.07 (m, 5H), 4.23 – 4.10 (m, 2H), 4.01 – 3.87 (m, 2H), 3.73 (s, 3H), 3.42 (d, J = 14.1 Hz, 1H), 3.32 (d, J = 14.1 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H), 1.08 (t, J = 7.1 Hz, 3H) ppm.; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.89, 154.78, 149.93, 147.27, 133.48, 131.23, 127.65, 126.85, 95.44, 63.59, 63.05, 53.23, 41.16, 14.27, 14.11 ppm; ES-HRMS Calcd for $C_{17}H_{21}N_3O_6$ $[M + Na]^+$ 386.1328, Found: 386.1327.



	Retention Time	% Area
1	8.962	49.58
2	12.898	50.42

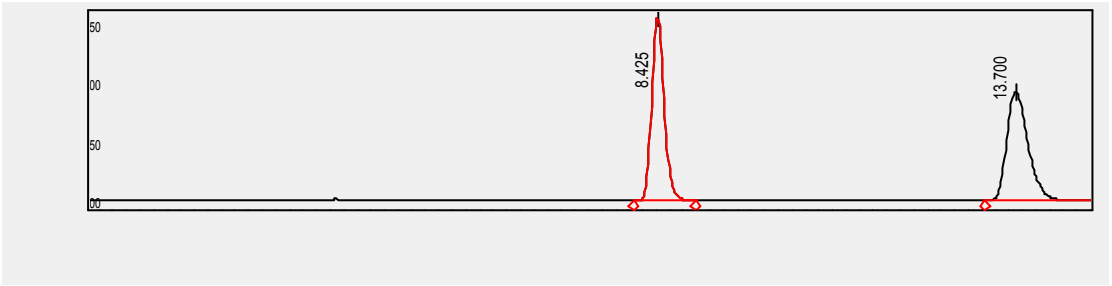
	Retention Time	% Area
1	8.790	90.05
2	12.718	9.95

triethyl 3-benzyl-3H-1,2,4-triazole-1,2,3-tricarboxylate (3ca)

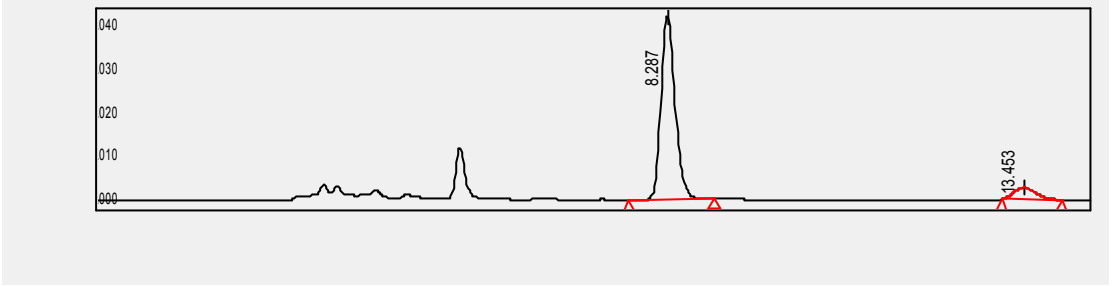


Prepared according to procedure **A**. The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 8:1 – 4:1) as yellow oil in 80% yield with 81% ee. $[\alpha]^{23}_{D}$ = 6.1 (c = 0.830, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel AD-H column. Eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (major) = 8.26 min, t_r (minor) = 13.45 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.17 – 7.06 (m, 5H), 4.24 – 4.09 (m, 4H), 3.95 (dddd, J = 22.0, 10.6, 7.2, 3.5 Hz, 2H), 3.42 (dd, J = 14.1, 4.5 Hz, 1H), 3.32 (d, J = 14.1 Hz, 1H), 1.23 (t, J = 7.1 Hz, 6H), 1.09 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.36, 154.76, 150.01, 147.19, 133.63, 131.22, 127.63, 126.81, 95.46, 63.56, 62.93, 62.62, 41.09, 14.34, 14.11, 13.81 ppm; ES-HRMS Calcd for $C_{18}H_{23}N_3O_6$ $[M + Na]^+$ 400.1485, Found: 400.1488.

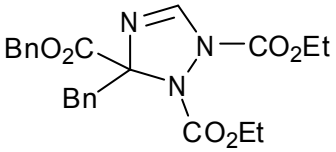


	Retention Time	% Area
1	8.425	50.08
2	13.700	49.92



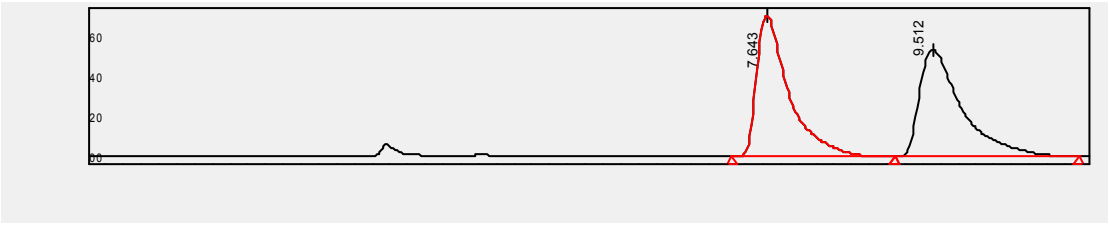
	Retention Time	% Area
1	8.287	90.68
2	13.453	9.32

3-benzyl 1,2-diethyl 3-benzyl-3H-1,2,4-triazole-1,2,3-tricarboxylate (3aa)

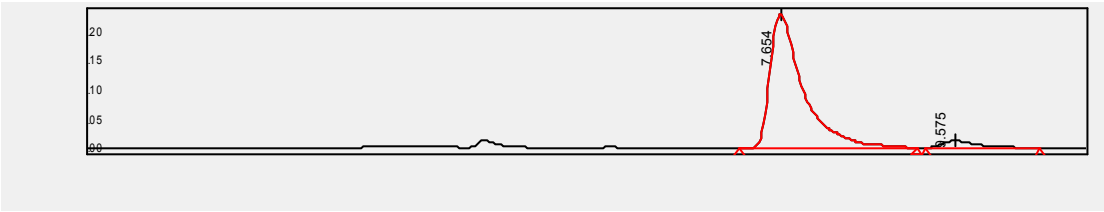


Prepared according to procedure **A**. The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 8:1 – 4:1) as yellow oil in 97% yield with 89% ee. $[\alpha]^{23}_D$ = 8.5 (c = 0.426, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel AD-H column. Eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (major) = 7.65 min, t_r (minor) = 9.57 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.28 (d, J = 3.6 Hz, 5H), 7.15 – 7.04 (m, 5H), 5.15 (s, 2H), 3.94 (dddd, J = 20.7, 17.0, 12.1, 7.0 Hz, 4H), 3.45 (d, J = 14.1 Hz, 1H, 3.34 (d, J = 14.1 Hz, 1H), 1.08 (td, J = 7.1, 3.9 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.24, 154.60, 149.99, 147.38, 134.80, 133.53, 131.23, 128.62, 128.54, 128.34, 127.65, 126.85, 95.45, 68.07, 63.55, 62.91, 41.14, 14.13, 14.11 ppm; ES-HRMS Calcd $C_{23}H_{25}N_3O_6$ $[M + Na]^+$ 462.1641, Found: 462.1641.

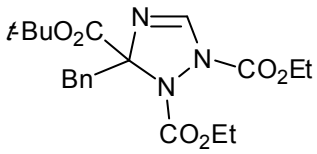


	Retention Time	% Area
1	7.643	49.97
2	9.512	50.03



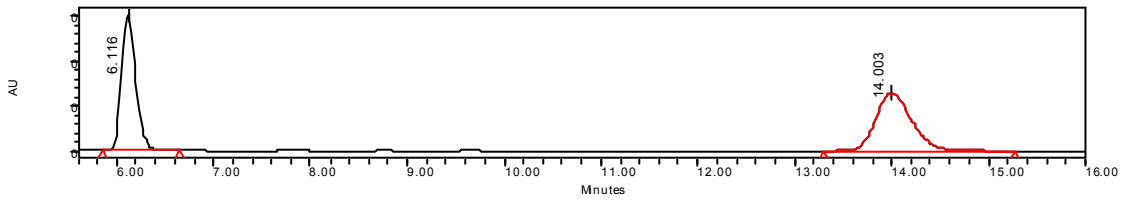
	Retention Time	% Area
1	7.654	94.84
2	9.575	5.16

3-tert-butyl 1,2-diethyl 3-benzyl-3H-1,2,4-triazole-1,2,3-tricarboxylate (3ka)

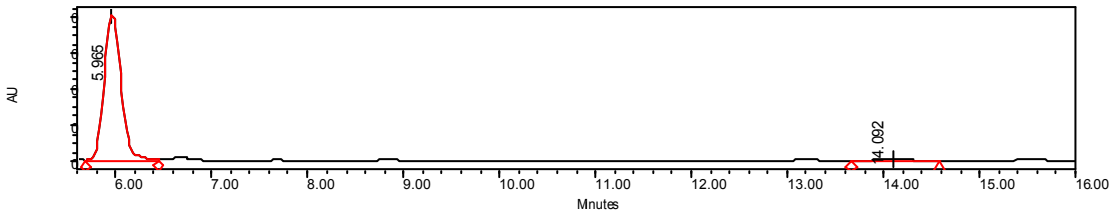


Prepared according to procedure **B**. The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 10:1 – 4:1) as yellow oil in 91% yield with 94% ee. $[\alpha]^{23}_{D}$ = 9.5 (c = 0.428, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel AD-H column. Eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (major) = 5.96 min, t_r (minor) = 14.09 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.16 – 7.07 (m, 5H), 4.35 – 4.21 (m, 1H), 4.17 – 4.05 (m, 1H), 4.04 – 3.86 (m, 2H), 3.41 (d, J = 14.1 Hz, 1H), 3.28 (d, J = 14.1 Hz, 1H), 1.42 (s, 9H), 1.25 (t, J = 7.1 Hz, 3H), 1.08 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.15, 154.78, 150.21, 146.89, 134.03, 131.16, 127.59, 126.69, 96.10, 83.51, 63.48, 62.77, 40.92, 27.69, 14.25, 14.10 ppm; ES-HRMS Calcd for $C_{20}H_{27}N_3O_6$ $[M + Na]^+$ 428.1798, Found: 428.1795.

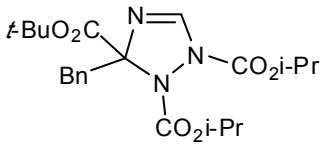


	Retention Time	% Area
1	6.116	48.27
2	14.003	51.73



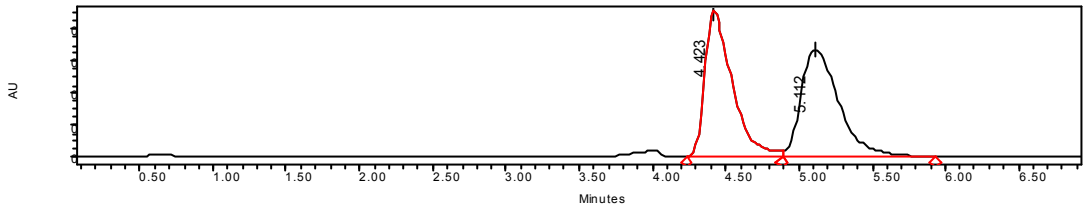
	Retention Time	% Area
1	5.965	96.94
2	14.092	3.06

3-tert-butyl 1,2-diisopropyl 3-benzyl-3H-1,2,4-triazole-1,2,3-tricarboxylate (3kb)

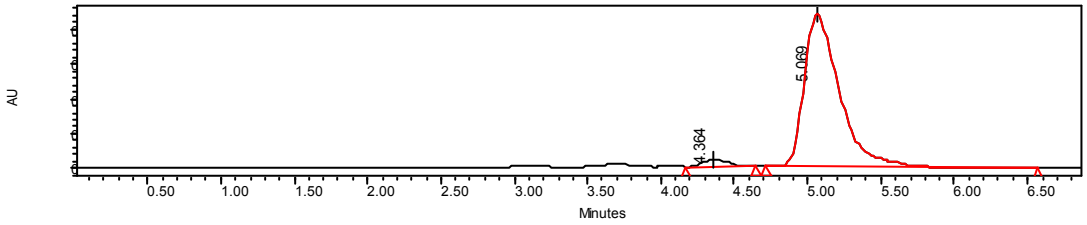


Prepared according to procedure **C**. The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 10:1 – 4:1) as yellow oil in 86% yield with 93% ee. $[\alpha]^{23}_{D}$ = 10.0 (c = 0.644, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column. Eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (minor) = 4.36 min, t_r (major) = 5.07 min.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.15 (d, *J*= 11.0 Hz, 5H), 4.98 (dt, *J*= 12.5, 6.2 Hz, 1H), 3.48 (d, *J*= 14.1 Hz, 1H), 3.34 (d, *J*= 14.1 Hz, 1H), 1.48 (s, 9H), 1.31 (dd, *J*= 11.2, 6.2 Hz, 6H), 1.17 (d, *J*= 6.3 Hz, 3H), 1.07 (d, *J*= 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.20, 154.39, 149.62, 146.85, 134.13, 131.08, 127.54, 126.58, 95.88, 83.34, 71.82, 71.04, 40.86, 27.67, 22.081, 21.61, 21.55, 21.51 ppm; ES-HRMS Calcd for $C_{22}H_{31}N_3O_6$ $[M + Na]^+$ 456.2111, Found: 456.2122.

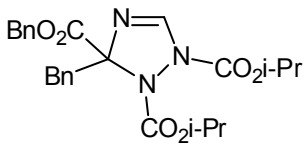


	Retention Time	% Area
1	4.423	49.25
2	5.112	50.75



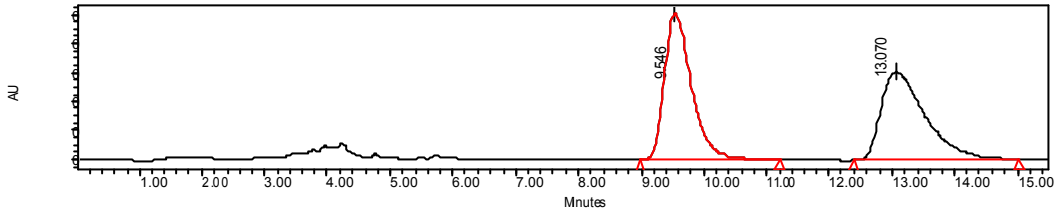
	Retention Time	% Area
1	4.364	3.32
2	5.069	96.68

3-benzyl 1,2-diisopropyl 3-benzyl-3H-1,2,4-triazole-1,2,3-tricarboxylate (3ab)

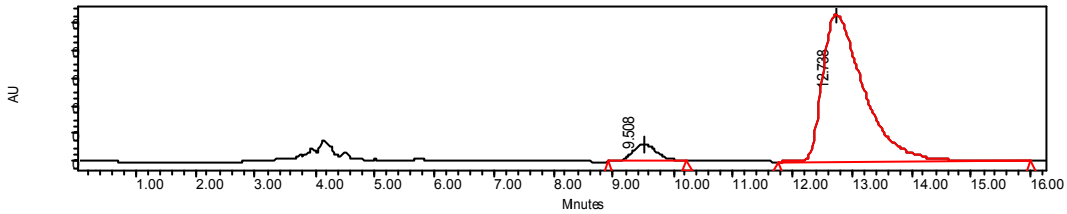


Prepared according to procedure **C**. The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 10:1 – 4:1) as yellow oil in 87% yield with 87% ee. $[\alpha]^{23}_{D}$ = 7.5 (c = 0.770, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel OD-H column. eluent: Hexane/Isopropanol = 95/5; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (minor) = 9.05 min, t_r (minor) = 12.74 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.21 (m, 6H), 7.26 (dd, *J* = 12.2, 5.3 Hz, 5H), 7.15 – 7.05 (m, 5H), 5.20 (d, *J* = 12.7 Hz, 1H), 5.09 (d, *J* = 12.4 Hz, 1H), 4.85 – 4.75 (m, 1H), 4.73 – 4.62 (m, 1H), 3.46 (d, *J* = 14.1 Hz, 1H), 3.46 (d, *J* = 14.1 Hz, 1H), 3.35 (d, *J* = 14.1 Hz, 1H), 1.15 (d, *J* = 6.3 Hz, 3H), 1.13 – 1.07 (m, 6H), 1.00 (t, *J* = 7.8 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.37, 147.41, 134.83, 133.69, 131.22, 128.60, 128.44, 128.09, 127.69, 126.83, 95.34, 72.05, 71.29, 67.96, 41.17, 21.91, 21.63, 21.60 ppm; ES-HRMS Calcd for $C_{25}H_{29}N_3O_6$ [M + Na]$^+$ 490.1954, Found: 490.1957.

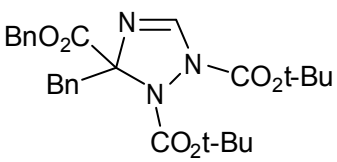


	Retention Time	% Area
1	9.546	50.07
2	13.070	49.93



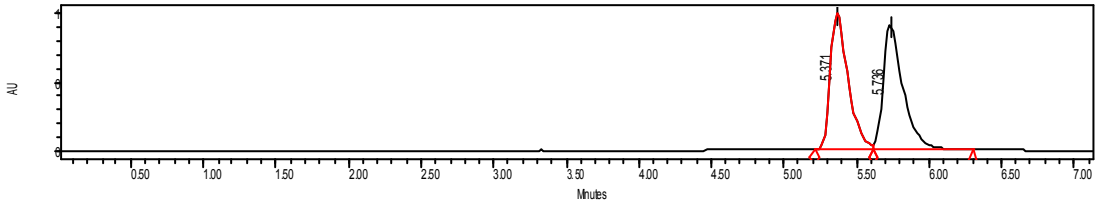
	Retention Time	% Area
1	9.508	6.69
2	12.738	93.31

3-benzyl 1,2-di-tert-butyl 3-benzyl-3H-1,2,4-triazole-1,2,3-tricarboxylate (3ac)

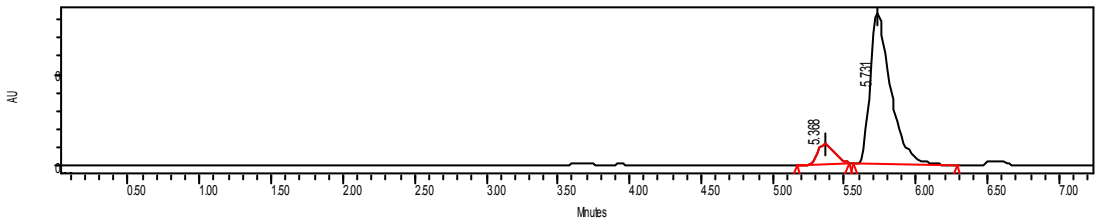


Prepared according to procedure **C**. The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 8:1 – 4:1) as yellow oil in 72% yield with 81% ee. $[\alpha]^{23}_{D}$ = 8.1 (c = 0.472, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column. Eluent: Hexane/Isopropanol = 95/5; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (minor) = 5.36 min, t_r (major) = 5.73 min.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 6H), 7.23 – 7.15 (m, 5H), 5.37 (d, J = 12.5 Hz, 1H), 5.08 (d, J = 12.5 Hz, 1H), 3.52 (d, J = 14.1 Hz, 1H), 3.41 (d, J = 14.1 Hz, 1H), 1.44 (s, 9H), 1.32 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.70, 147.74, 134.88, 133.92, 131.17, 131.17, 128.50, 128.27, 127.90, 127.64, 127.64, 126.71, 83.91, 82.98, 67.74, 41.14, 27.93, 27.68 ppm; ES-HRMS Calcd for $C_{27}H_{33}N_3O_6$ $[M + H]^+$ 496.2448, Found: 496.2438.

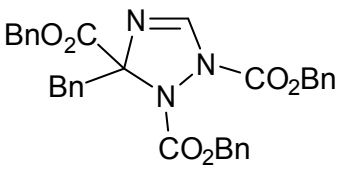


	Retention Time	% Area
1	5.371	49.89
2	5.736	50.11



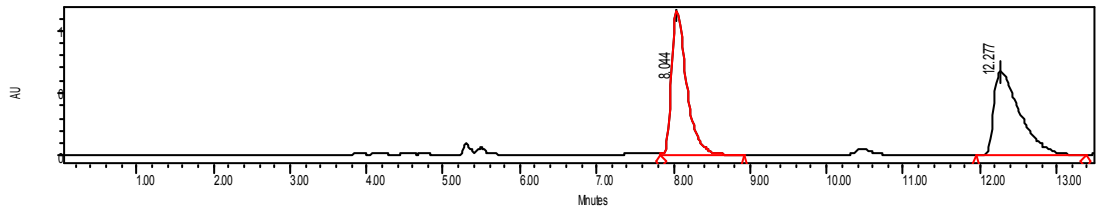
	Retention Time	% Area
1	5.368	9.33
2	5.731	90.67

Tribenzyl 3-benzyl-3H-1,2,4-triazole-1,2,3-tricarboxylate (3ad)

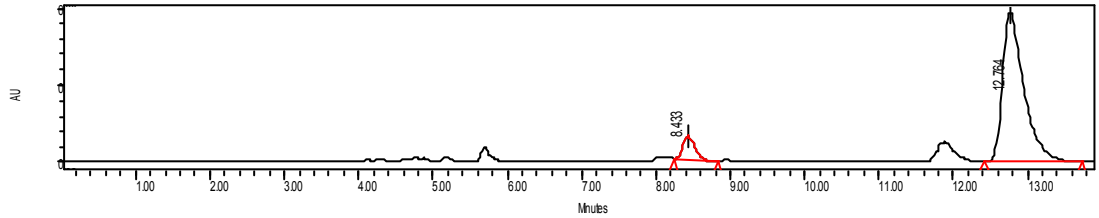


Prepared according to procedure **C**. The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 8:1) as yellow oil in 94% yield with 84% ee. $[\alpha]^{23}_D$ = 4.4 (c = 0.594, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column. Eluent: Hexane/Isopropanol = 95/5; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (minor) = 8.43 min, t_r (major) = 12.76 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dt, J = 32.5, 10.6 Hz, 13H), 7.19 – 7.08 (m, 7H), 5.12 – 4.82 (m, 6H), 3.51 (d, J = 14.2 Hz, 1H), 3.40 (d, J = 14.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.04, 154.50, 149.93, 147.16, 134.98, 134.76, 134.37, 133.31, 131.16, 128.70, 128.64, 128.61, 128.51, 128.48, 128.31, 128.26, 127.69, 127.01, 126.91, 95.61, 69.07, 68.44, 67.97, 41.07 ppm; ES-HRMS Calcd for $C_{33}H_{29}N_3O_6$ $[M + Na]^+$ 586.1954, Found: 586.1948.

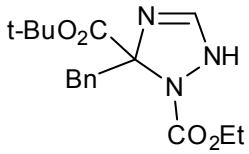


	Retention Time	% Area
1	8.044	50.30
2	12.277	49.70



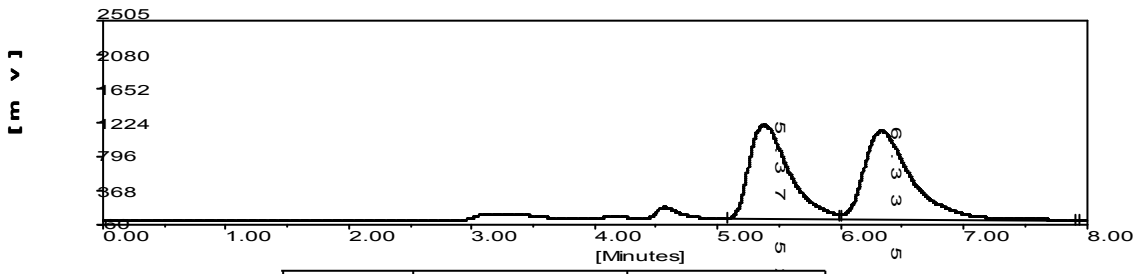
	Retention Time	% Area
1	8.433	7.89
2	12.764	92.11

5-tert-butyl 1-ethyl 5-benzyl-2H-1,2,4-triazole-1,5(5H)-dicarboxylate (4a)

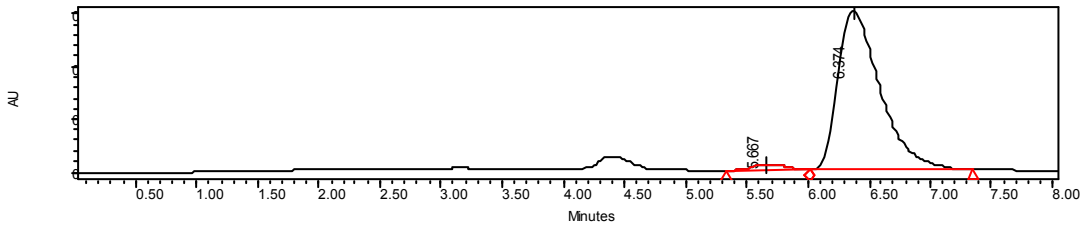


The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 2:1) as white solid in 70% yield with 94% ee. $[\alpha]^{23}_{D}$ = -2.2 (c = 0.172, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel OD-H column. Eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (minor) = 5.66 min, t_r (major) = 6.37 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 3H), 7.11 (d, J = 7.6 Hz, 2H), 6.42 (s, 1H), 5.21 (s, 1H), 4.39 – 4.16 (m, 2H), 3.57 (dd, J = 28.6, 22.4 Hz, 1H), 3.30 (d, J = 14.6 Hz, 1H), 1.44 – 1.38 (m, 9H), 1.33 – 1.25 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.36, 140.23, 134.48, 130.71, 128.26, 127.09, 83.18, 81.36, 62.07, 39.06, 27.80, 14.73 ppm; ES-HRMS Calcd for $C_{17}H_{23}N_3O_4$ $[M + Na]^+$ 356.1586, Found: 356.1584.

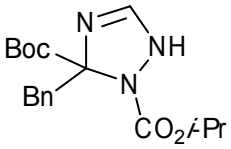


	Retention Time	% Area
1	5.37	49.55
2	6.33	50.45



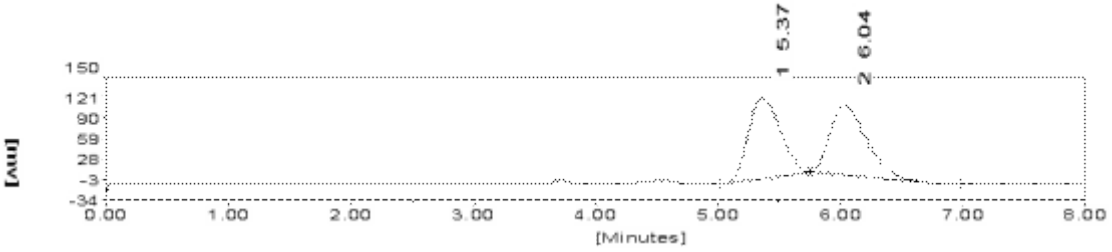
	Retention Time	% Area
1	5.667	2.98
2	6.374	97.02

5-tert-butyl 1-isopropyl 5-benzyl-2H-1,2,4-triazole-1,5(5H)-dicarboxylate (4b)

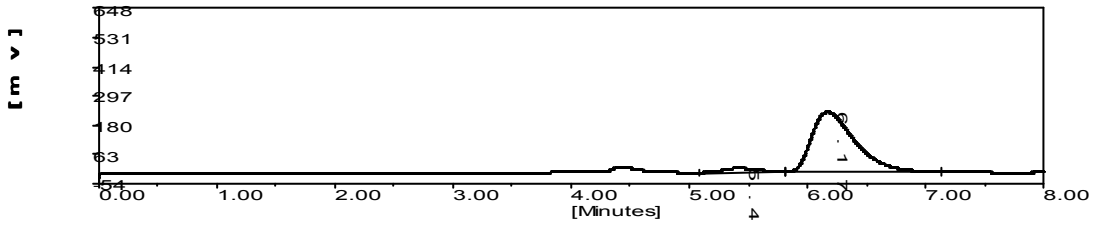


The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 2:1) as white solid in 73% yield with 91% ee. $[\alpha]^{23}_{D}$ = -4.1 (c = 0.302, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel OD-H column. Eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (minor) = 5.42 min, t_r (major) = 6.17 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 18.6, 6.9 Hz, 5H), 6.41 (s, 1H), 5.39 – 4.91 (m, 2H), 3.57 (d, *J* = 21.7 Hz, 1H), 3.36 – 3.18 (m, 1H), 1.40 (s, *J* = 12.3 Hz, 9H), 1.30 (d, *J* = 6.1 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.40, 140.09, 134.55, 130.71, 128.28, 127.09, 83.13, 81.31, 76.73, 69.81, 38.97, 27.82, 22.22, 22.10, 21.97 ppm; ES-HRMS Calcd for $C_{18}H_{25}N_3O_4$ $[M + H]^+$ 348.1923, Found: 348.1927.

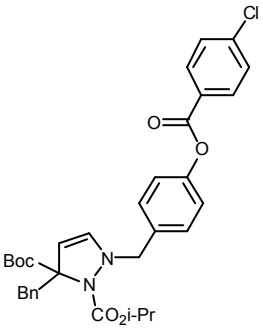


	Retention Time	% Area
1	5.37	52.09
2	6.04	47.98



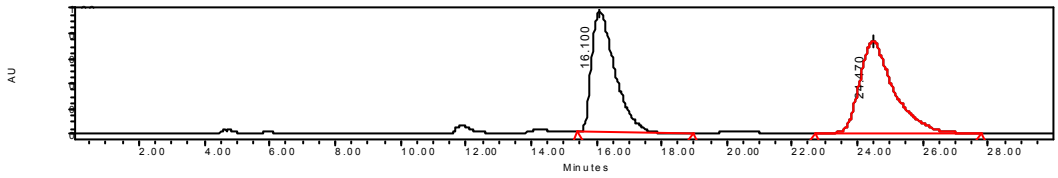
	Retention Time	% Area
1	5.43	4.8324
2	6.17	95.1676

5-tert-butyl 1-isopropyl 2-(4-(4-chlorobenzoyloxy)benzyl)-5-benzyl-2H-pyrazole-1,5(5H)-dicarboxylate (5a)

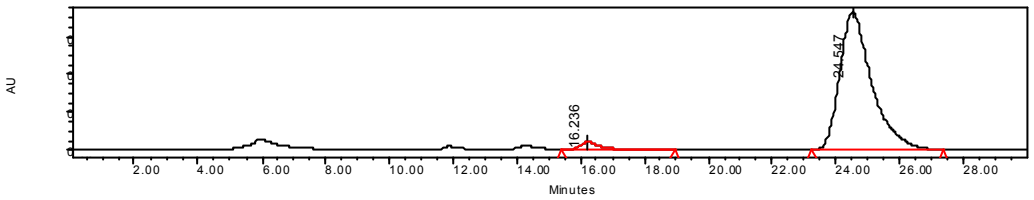


The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as yellow oil in 65% yield with 91% ee. $[\alpha]^{23}_D$ = 8.4 (c = 0.256, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel AD-H column. Eluent: Hexane/Isopropanol = 80/20; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (minor) = 16.23 min, t_r (major) = 24.54 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.31 (dd, *J* = 13.7, 6.9 Hz, 3H), 7.14 (d, *J* = 15.2 Hz, 6H), 6.50 (s, *J* = 25.3 Hz, 1H), 5.30 (s, 1H), 5.06 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.33 (s, 1H), 4.12 (dd, *J* = 14.2, 7.1 Hz, 1H), 3.52 (d, *J* = 13.9 Hz, 1H), 3.36 (s, 1H), 1.51 (s, 9H), 1.40 (s, 3H), 1.33 (d, *J* = 6.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.50, 164.20, 154.28, 150.61,, 140.29, 131.56, 131.48, 130.611, 129.01, 127.78, 127.72, 126.90, 121.85, 95.47, 82.88, 70.26, 40.78, 27.85, 22.34, 21.98 ppm; ES-HRMS Calcd for $C_{32}H_{34}N_3O_6Cl$ [M + H]$^+$ 592.2214, Found: 502.2209.

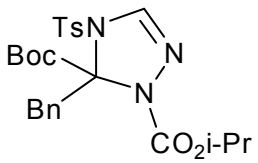


	Retention Time	% Area
1	16.100	48.33
2	24.470	51.67



	Retention Time	% Area
1	16.236	4.42
2	24.547	95.58

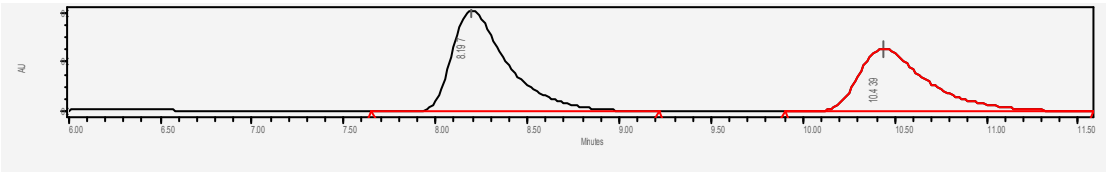
5-tert-butyl 1-isopropyl 5-benzyl-2-tosyl-2H-pyrazole-1,5(5H)-dicarboxylate (5b)



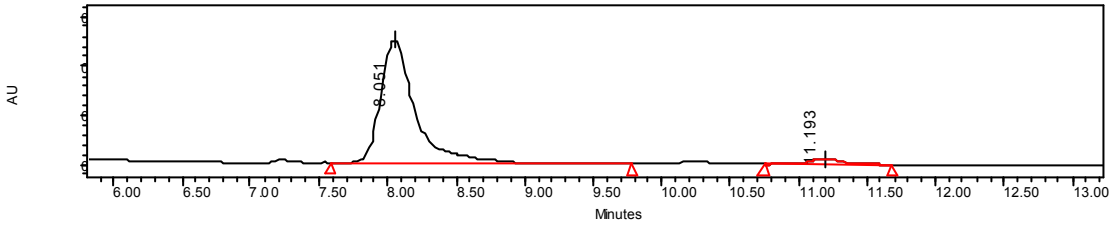
The crude product was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as yellow oil in 95% yield with 91% ee. $[\alpha]^{23}_D$ = 10.1 (c = 0.298, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IA column. Eluent: Hexane/Isopropanol = 85/15; Flow rate: 1.0 mL/min; λ = 254 nm; t_r (major) = 8.05 min, t_r (minor) = 10.19 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 10.1 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.21–7.06 (m,

5H), 6.75 (s, 1H), 5.09 – 4.97 (m, 1H), 3.79 (d, J = 15.1 Hz, 1H), 3.53 (dd, J = 15.0, 7.2 Hz, 1H), 2.45 (s, 3H), 1.43 – 1.39 (m, 9H), 1.35 (d, J = 6.2 Hz, 3H), 1.30 (d, J = 6.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.58, 150.57, 145.45, 136.02, 134.73, 133.86, 130.52, 130.02, 128.19, 127.65, 127.19, 85.48, 84.38, 70.64, 38.35, 27.61, 21.99, 21.65 ppm; ES-HRMS Calcd for $C_{25}H_{31}N_3O_6S$ $[M + H]^+$ 502.2012, Found: 502.2014.



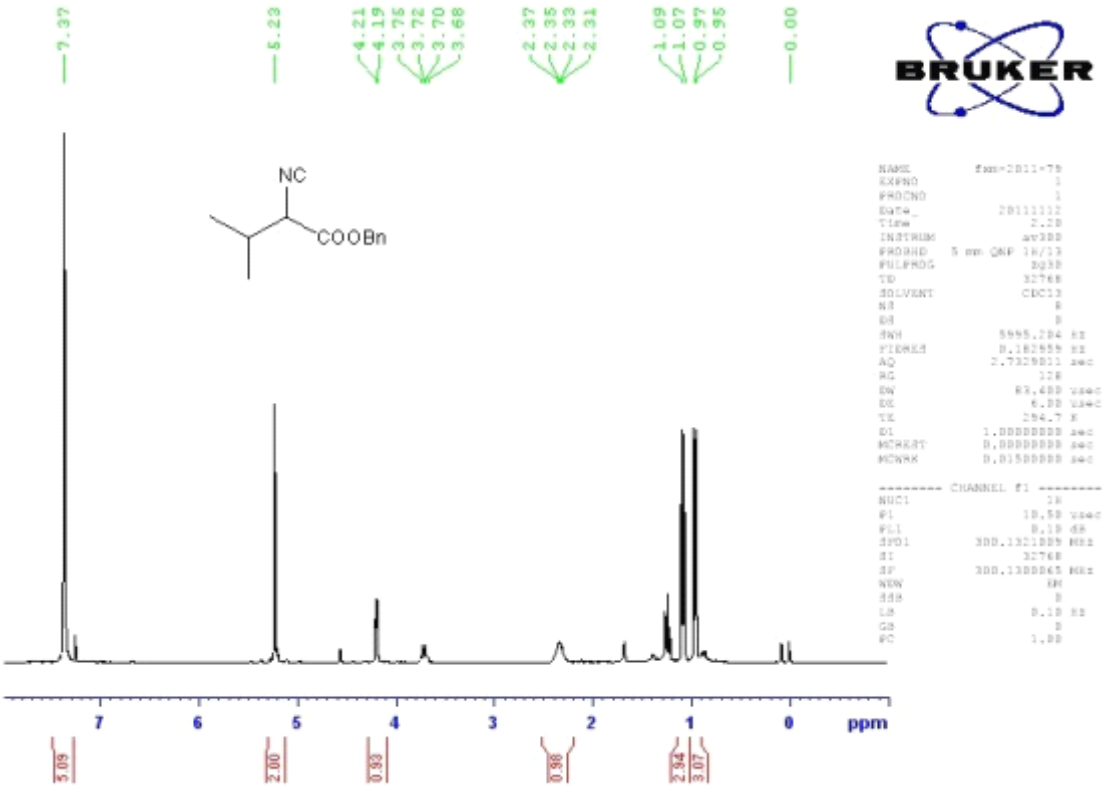
	Retention Time	% Area
1	7.764	53.95
2	10.367	46.05



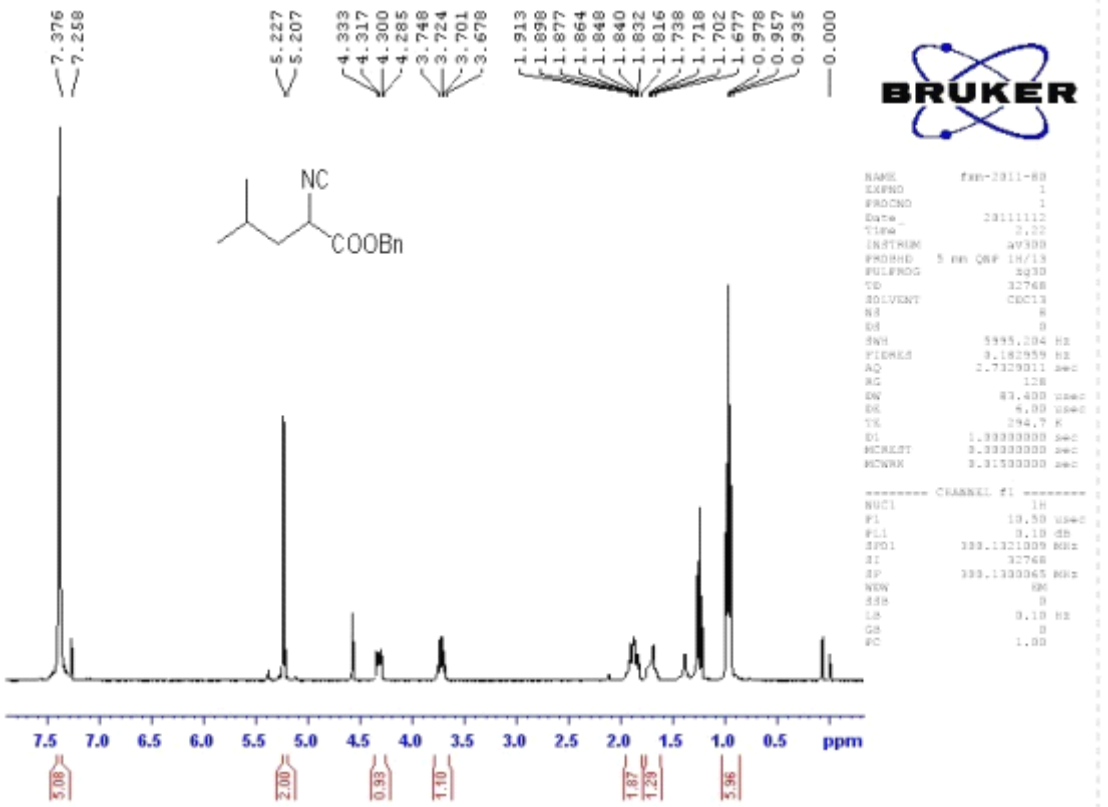
	Retention Time	% Area
1	8.051	95.59
2	11.193	4.41

I. Copies of NMR Spectra for isocyano esters

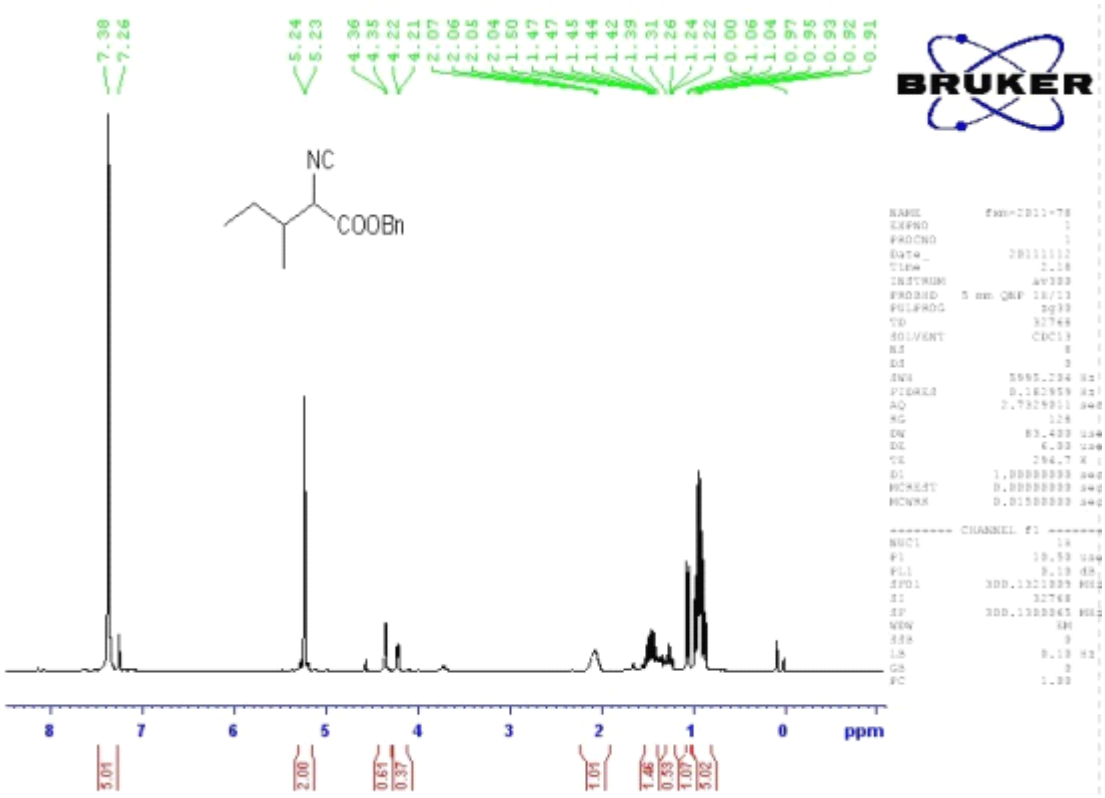
NMR for 1e



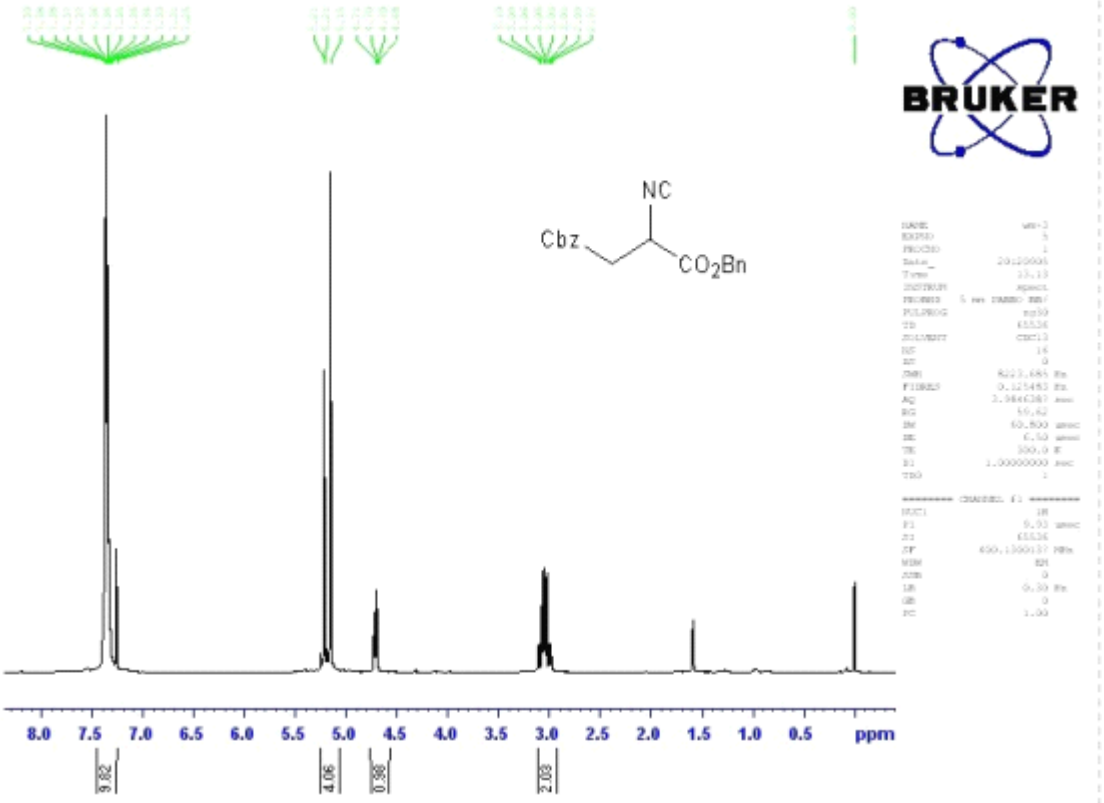
NMR for 1f



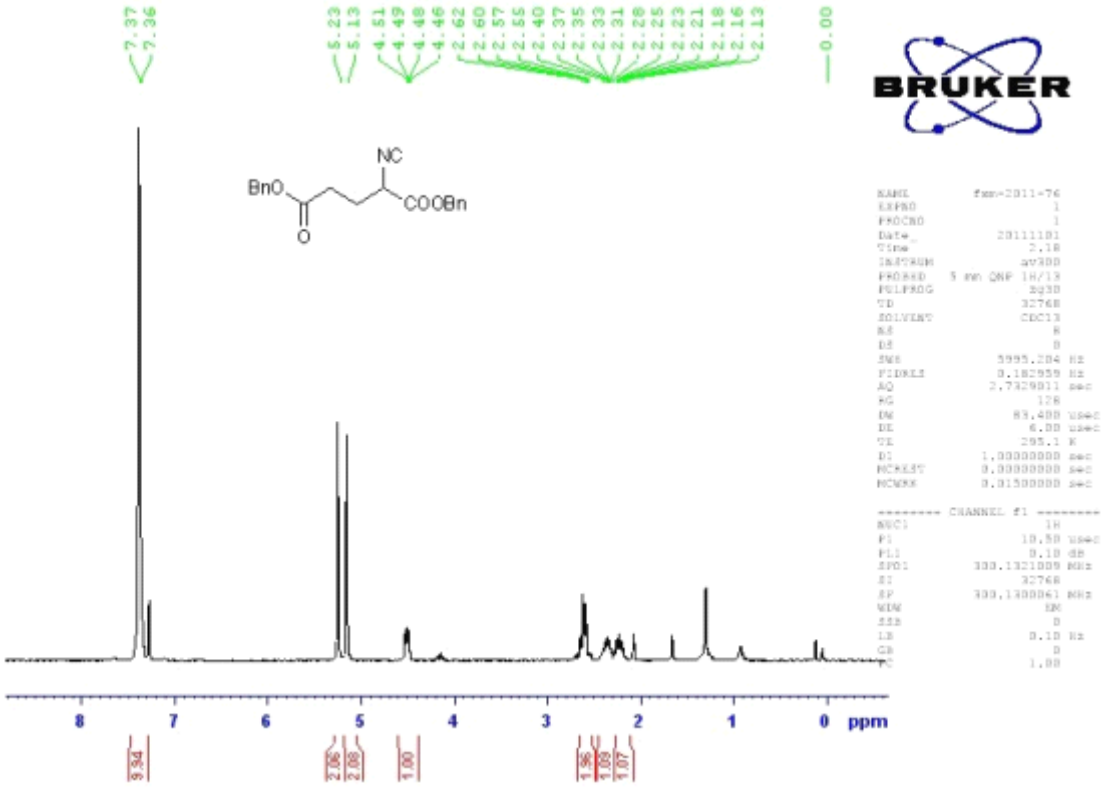
NMR for 1g



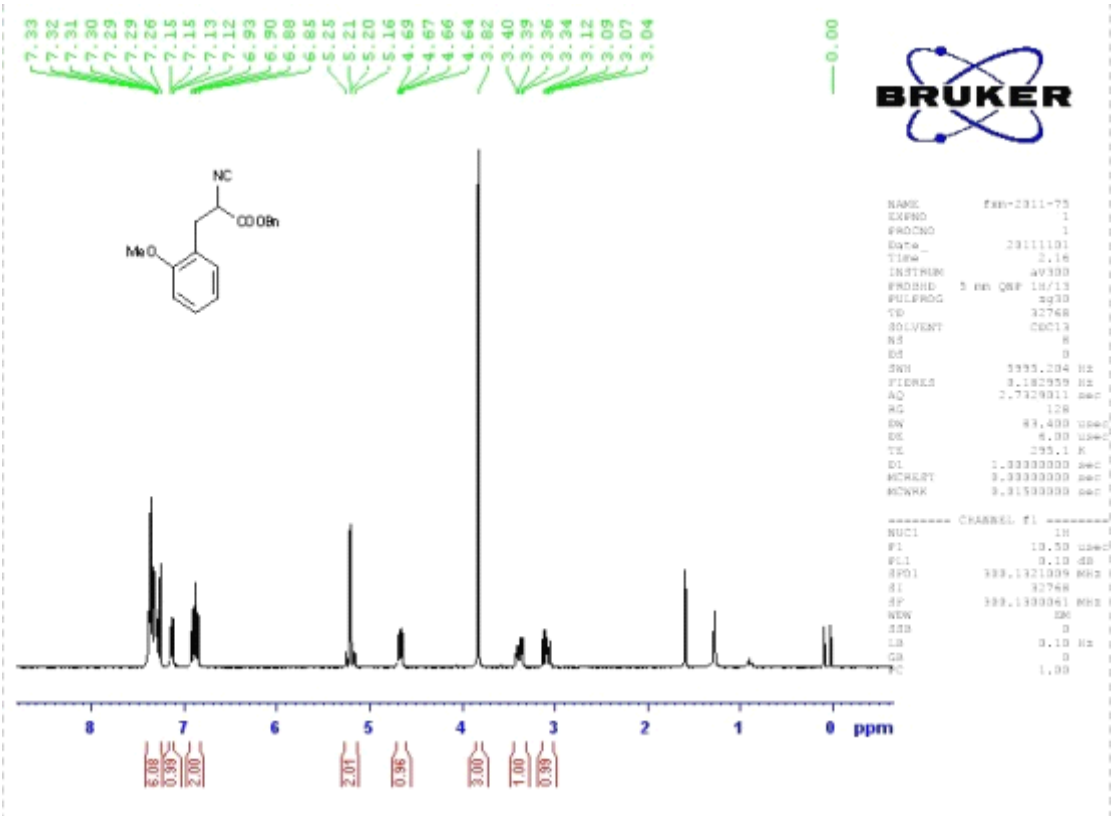
NMR for 1h



NMR for 1i

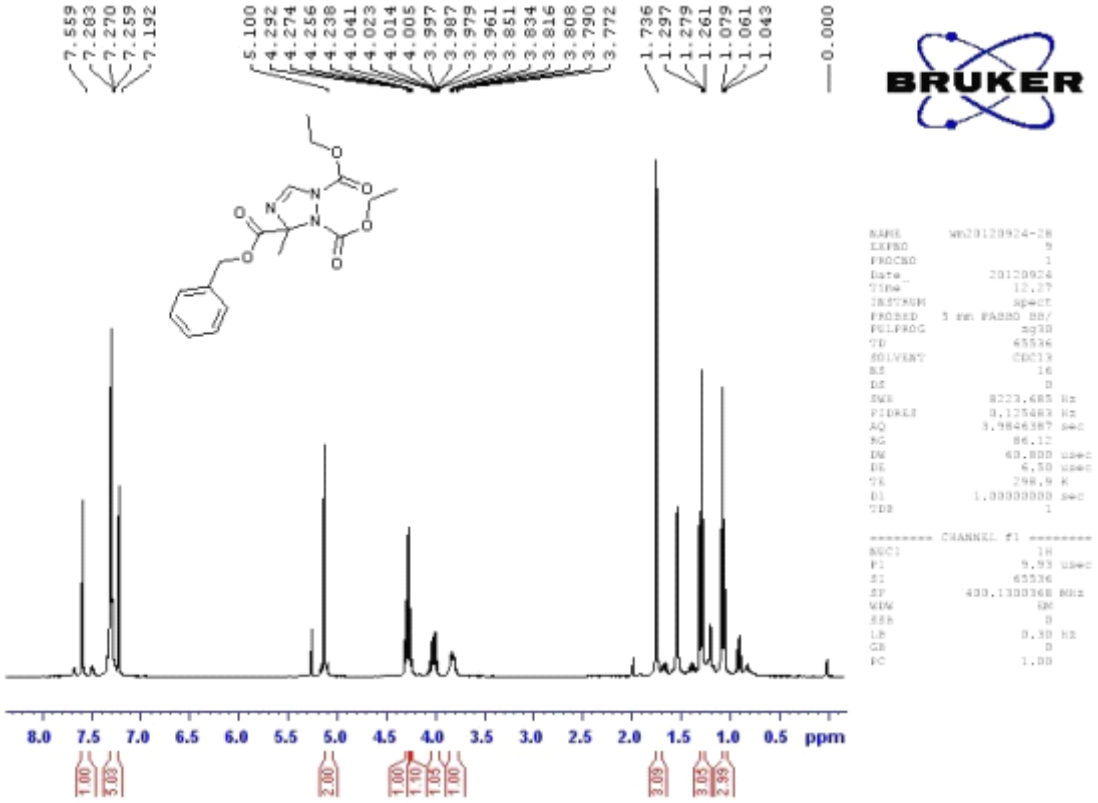


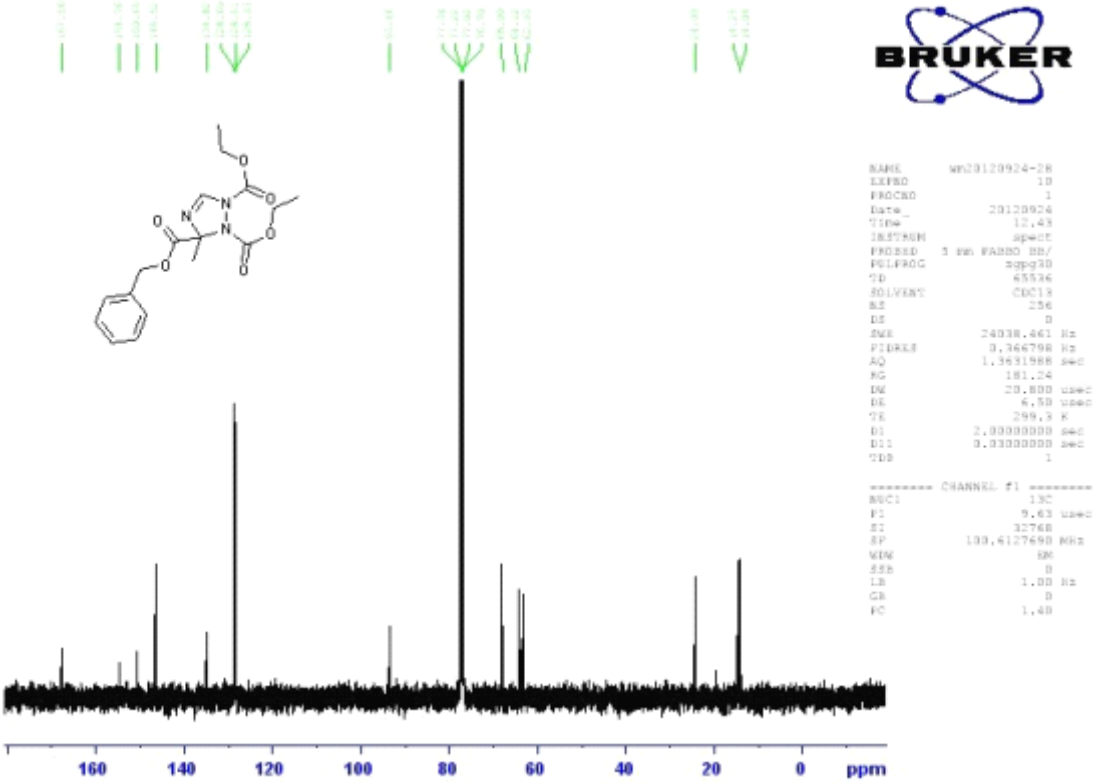
NMR for 1j



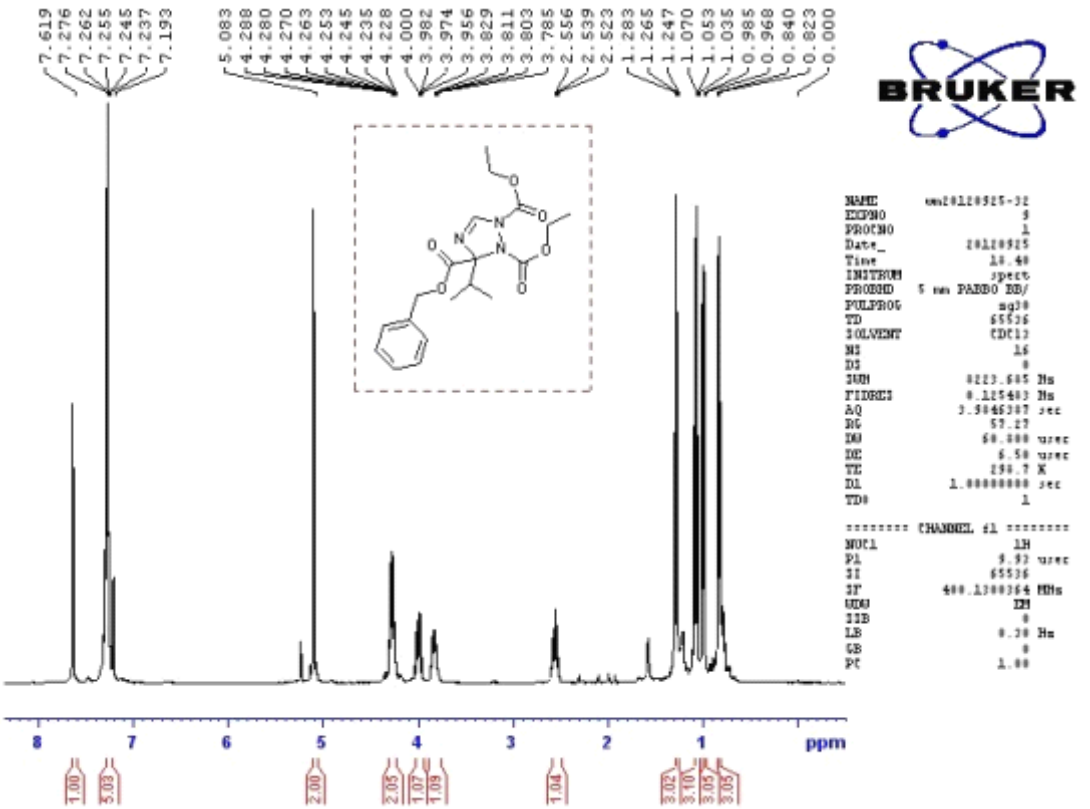
J. Copies of NMR Spectra for the compounds

NMR for 3da





NMR for 3ea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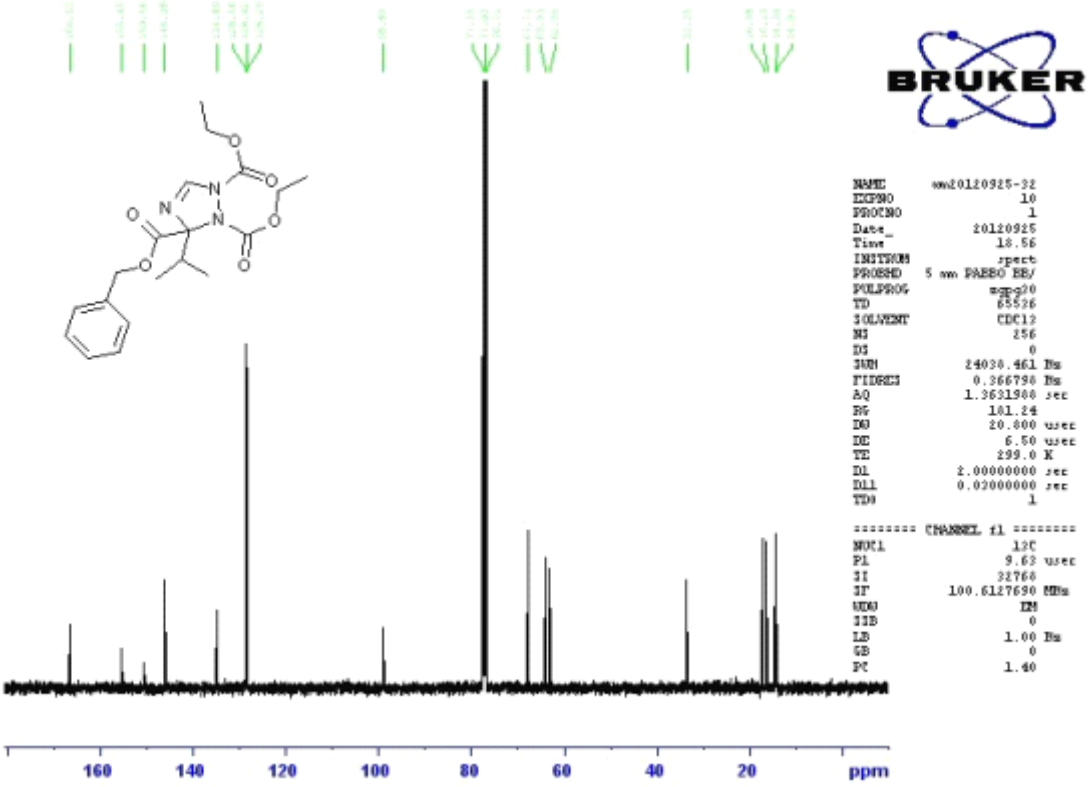
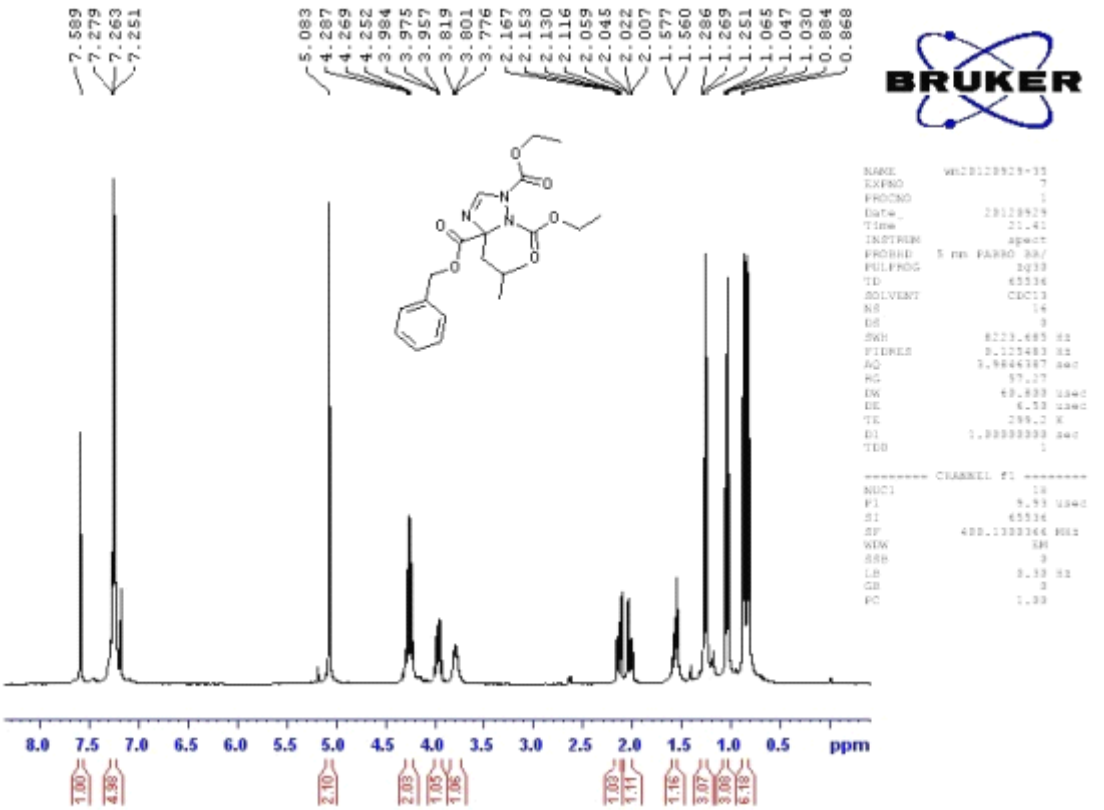
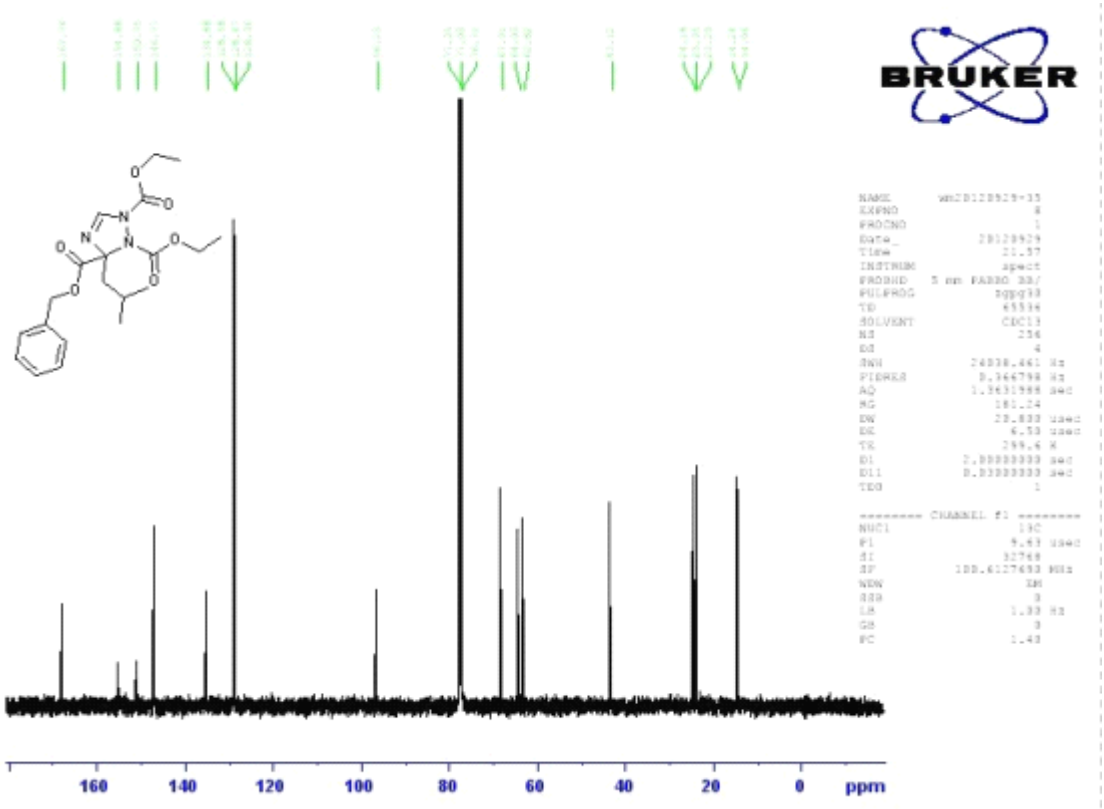
7.262
7.255
7.245
7.237
7.193
5.083
4.288
4.280
4.270
4.263
4.253
4.245
4.235
4.228
4.000
3.982
3.974
3.956
3.829
3.811
3.803
3.785
2.556
2.539
2.523
1.283
1.265
1.247
1.070
1.053
1.035
0.985
0.968
0.840
0.823
0.000
BRUKER
8
7
6
5
4
3
2
1
ppm
1.00
5.03
2.00
2.05
1.07
1.09
1.04
3.02
3.10
3.05
3.05

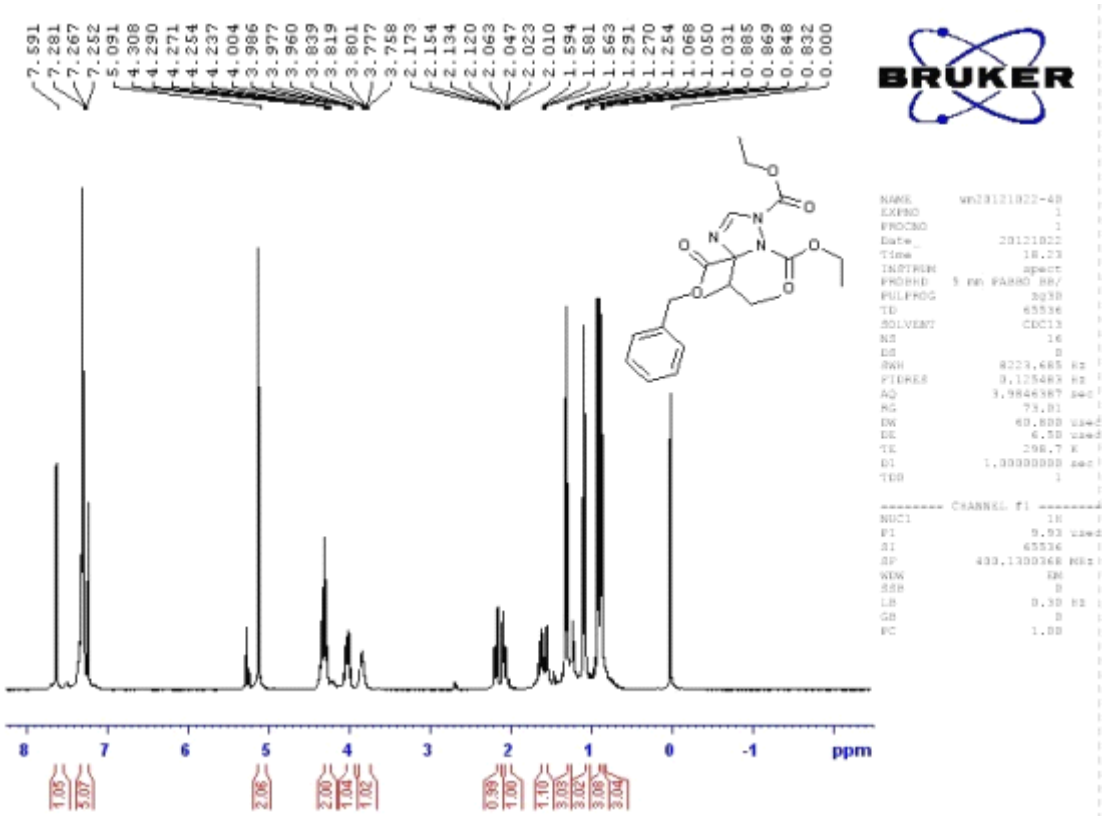

BRUKER
160
140
120
100
80
60
40
20
ppm

NMR for 3fa


7.589
7.279
7.263
7.251
5.083
4.287
4.269
4.252
3.984
3.975
3.957
3.819
3.801
3.776
2.167
2.153
2.130
2.116
2.059
2.045
2.022
2.007
1.577
1.560
1.286
1.269
1.251
1.065
1.047
1.030
0.884
0.868
BRUKER
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 4.38 2.10 2.05 1.05 1.06 1.03 1.11 1.16 3.07 3.00 6.18


BRUKER
160 140 120 100 80 60 40 20 0 ppm

NMR for 3ga


7.591
7.281
7.267
7.252
5.091
4.308
4.290
4.271
4.254
4.237
4.004
3.986
3.977
3.960
3.839
3.819
3.801
3.777
3.758
2.173
2.154
2.134
2.120
2.063
2.047
2.023
2.010
1.594
1.581
1.563
1.291
1.270
1.254
1.068
1.050
1.031
0.885
0.869
0.848
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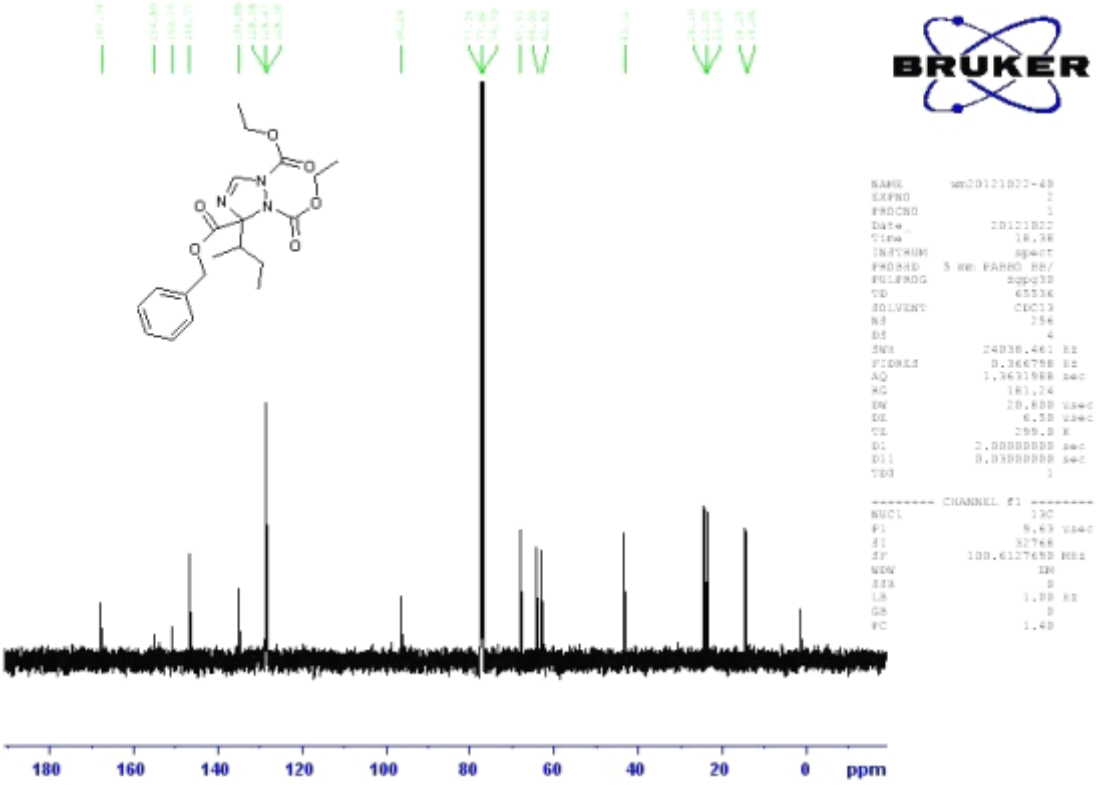
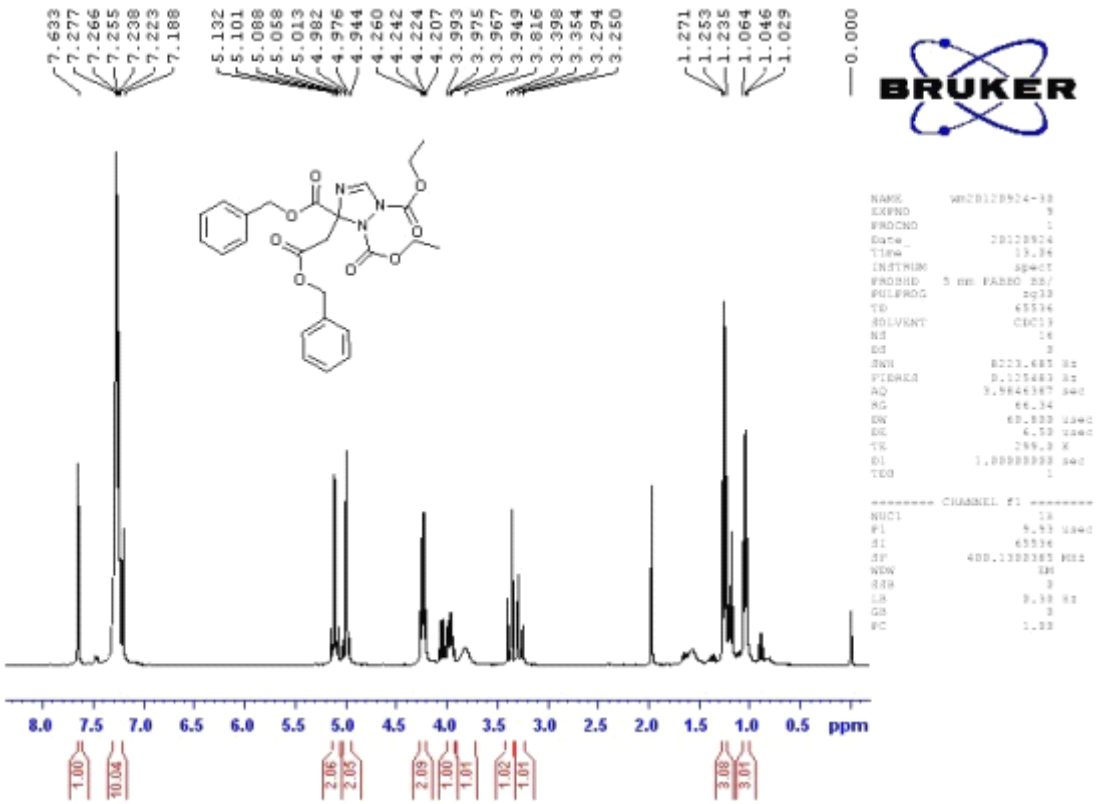
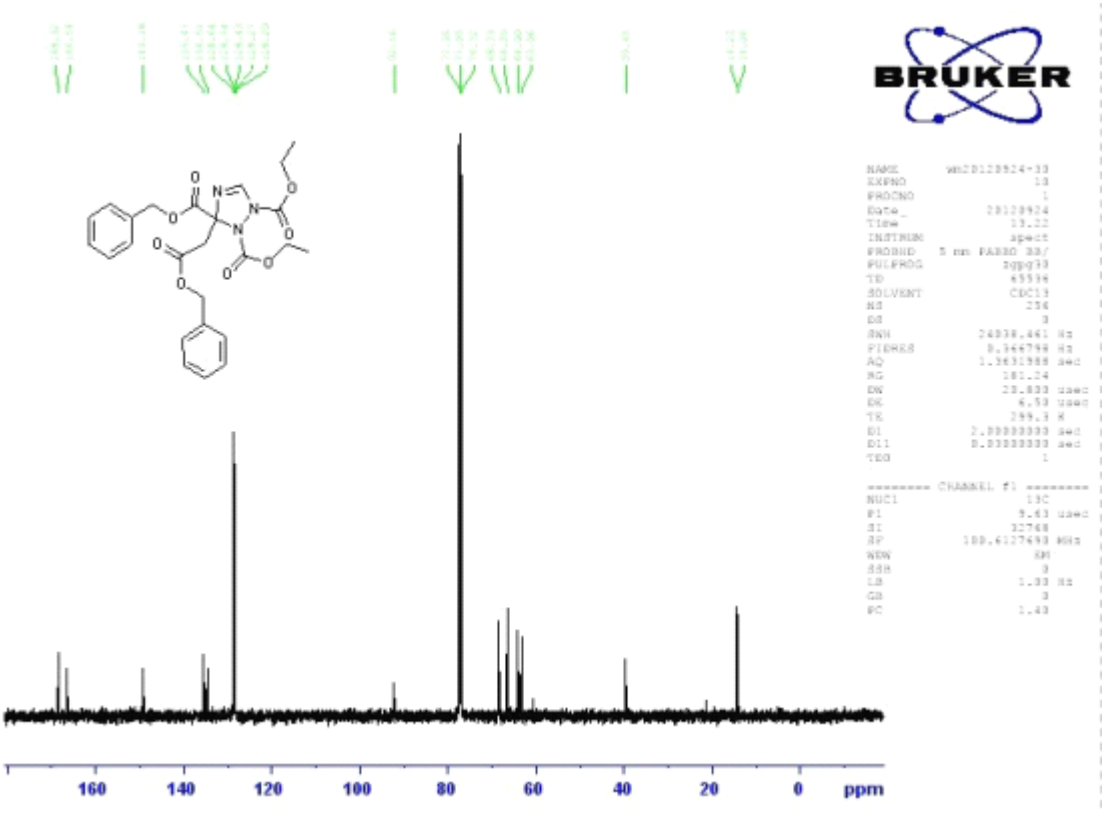
0.000
BRUKER
8
7
6
5
4
3
2
1
0
-1
ppm

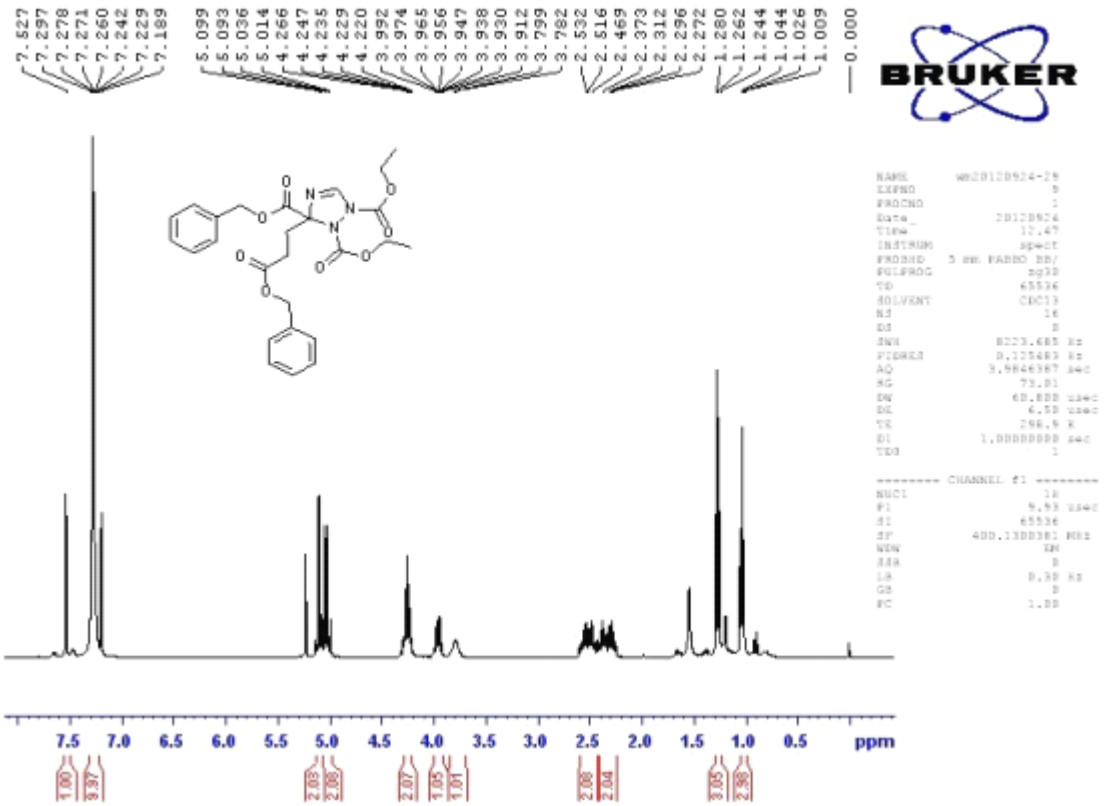

BRUKER
180
160
140
120
100
80
60
40
20
0
ppm

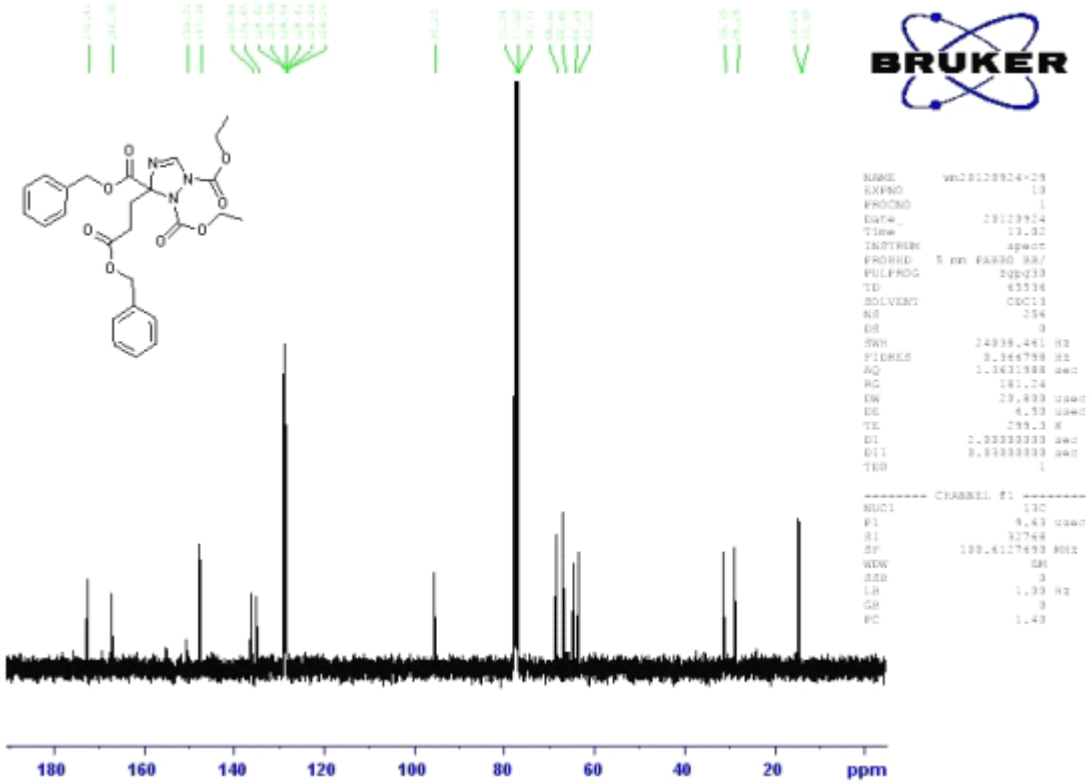
NMR for 3ha


7.633
7.277
7.266
7.255
7.238
7.223
7.188
5.132
5.101
5.088
5.058
5.013
4.982
4.976
4.944
4.260
4.242
4.224
4.207
3.993
3.975
3.967
3.949
3.816
3.398
3.354
3.294
3.250
1.271
1.253
1.235
1.064
1.046
1.029
0.000
BRUKER
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
10.04
2.06
2.03
2.09
1.00
1.01
1.02
1.01
3.08
3.01

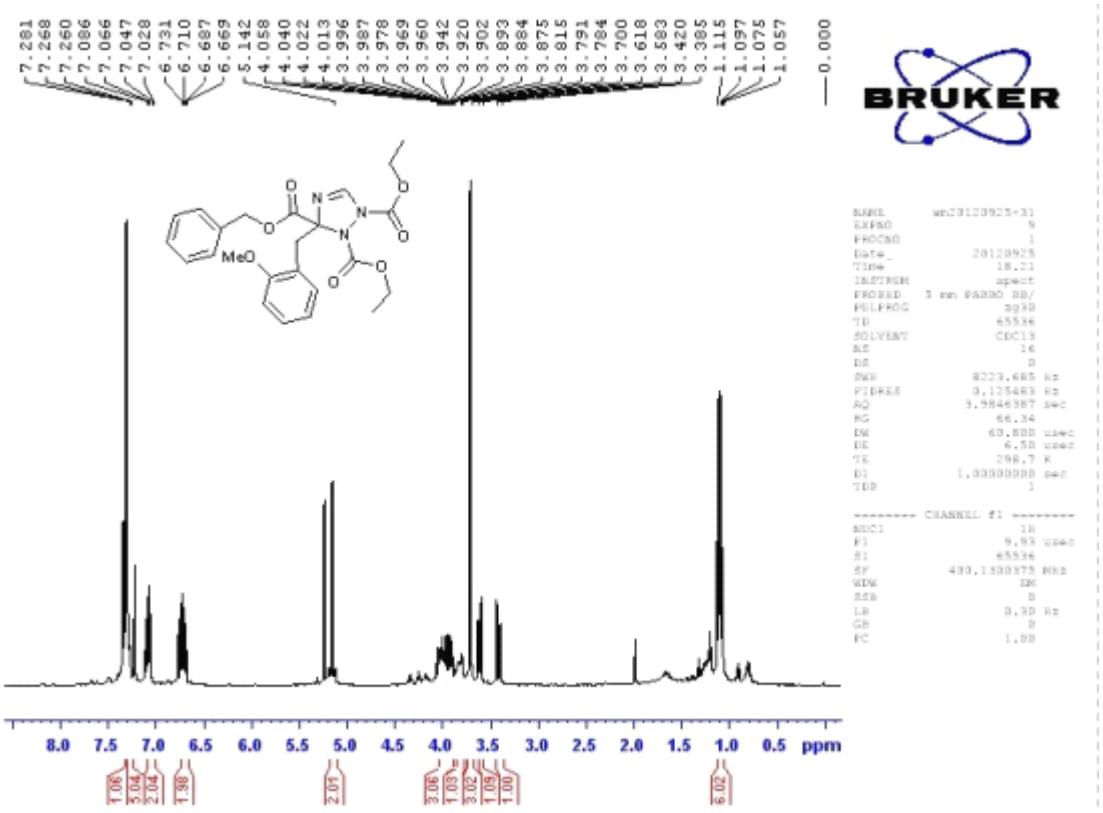

BRUKER
160 140 120 100 80 60 40 20 0 ppm

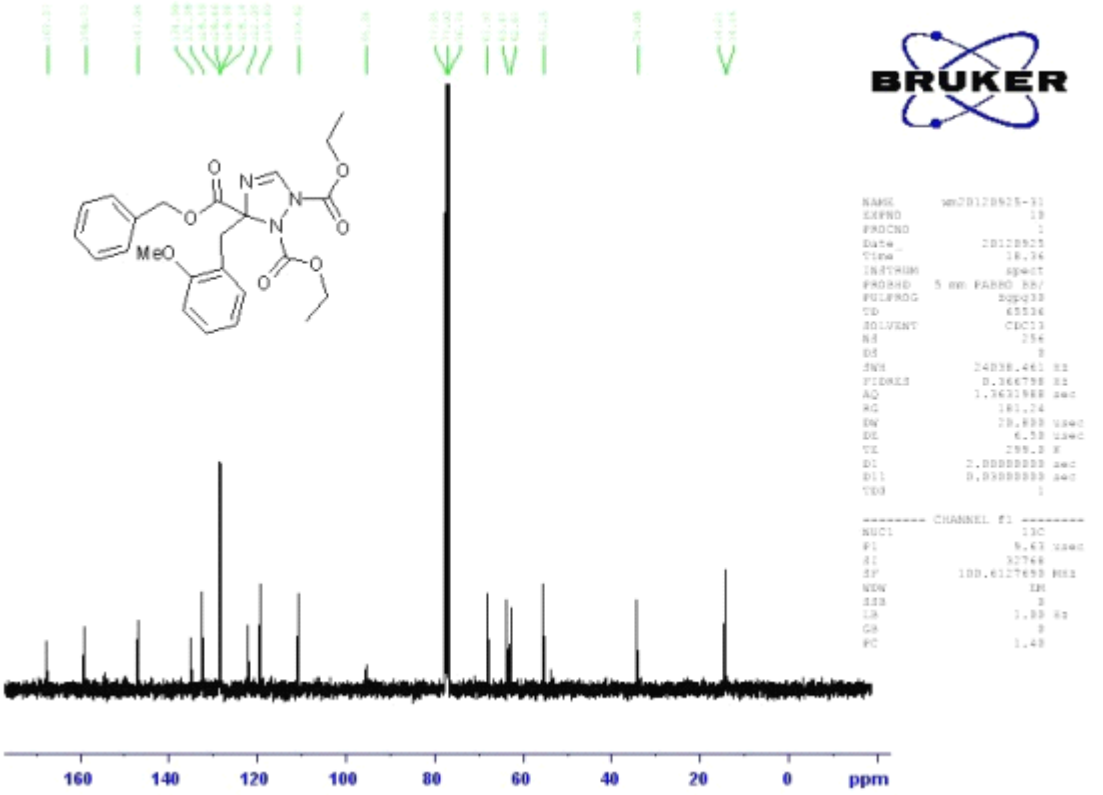
NMR for 3ia


7.527
7.297
7.278
7.271
7.260
7.242
7.229
7.189
5.099
5.093
5.036
5.014
4.266
4.247
4.235
4.229
4.220
3.992
3.974
3.965
3.956
3.947
3.938
3.930
3.912
3.799
3.782
2.532
2.516
2.469
2.373
2.312
2.296
2.272
1.280
1.262
1.244
1.044
1.026
1.009
0.000
BRUKER
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 0.97 2.05 2.08 2.07 1.05 1.01 2.08 2.04 3.05 2.98

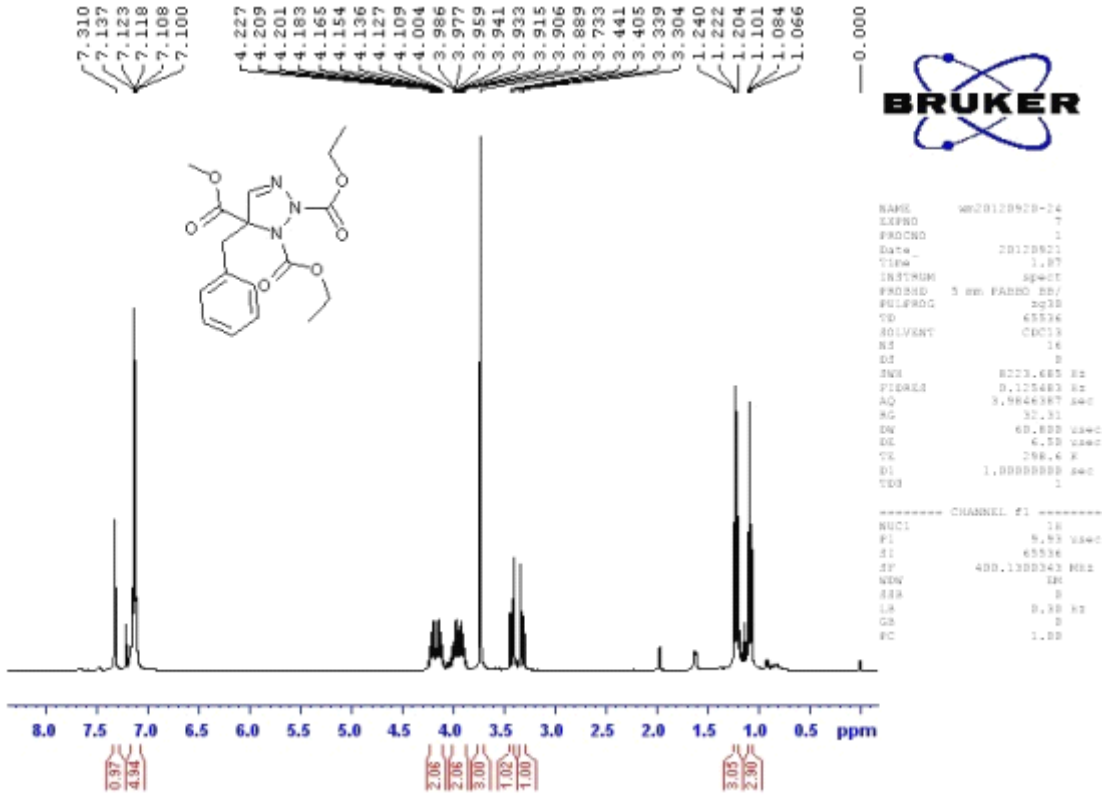

BRUKER
180 160 140 120 100 80 60 40 20 ppm

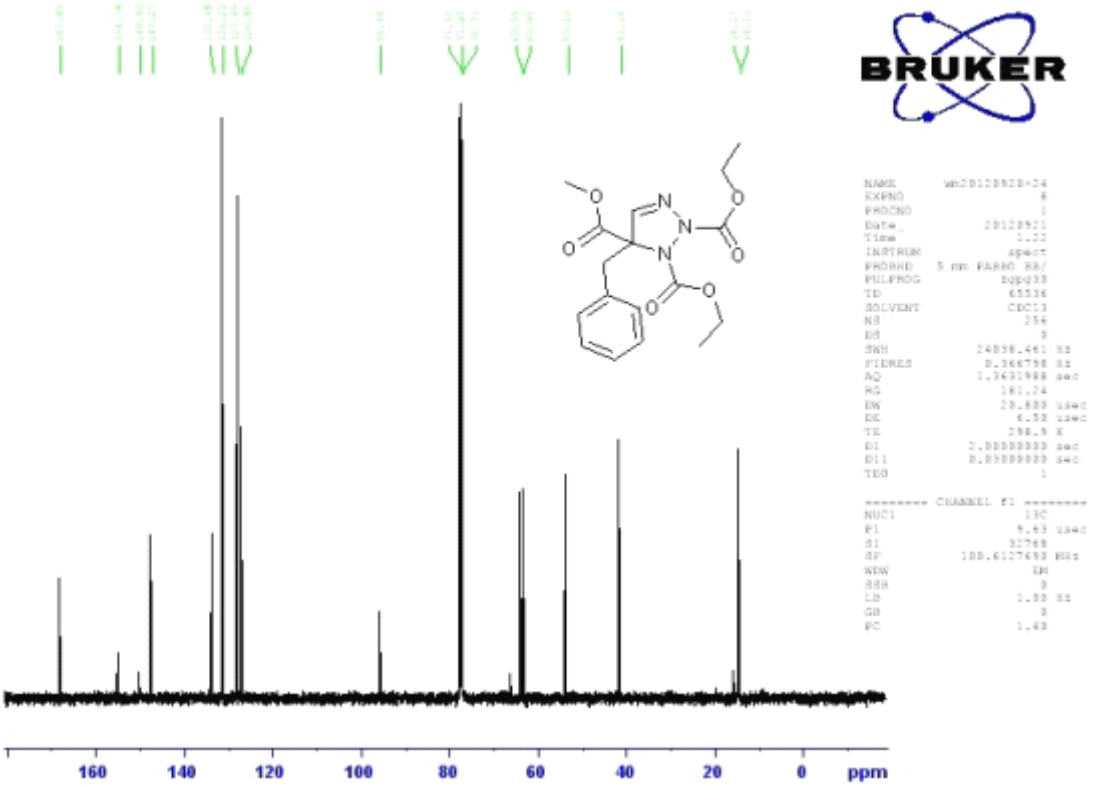
NMR for 3ja


7.281
7.268
7.260
7.086
7.066
7.047
7.028
6.731
6.710
6.687
6.669
5.142
4.058
4.040
4.022
4.013
3.996
3.987
3.978
3.969
3.960
3.942
3.920
3.902
3.893
3.884
3.875
3.815
3.791
3.784
3.700
3.618
3.583
3.420
3.385
1.115
1.097
1.075
1.057
0.000
MeO
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.06
3.04
2.04
1.98
2.01
3.06
1.03
3.02
1.09
1.00
6.02

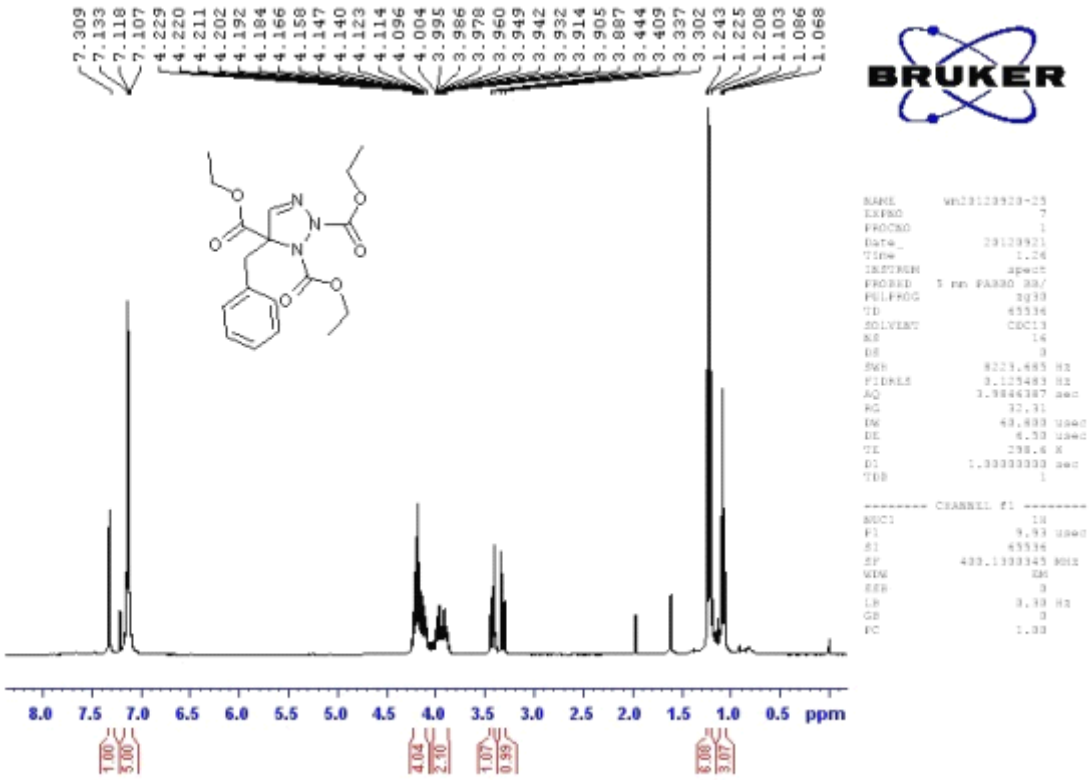

MeO
160 140 120 100 80 60 40 20 0 ppm

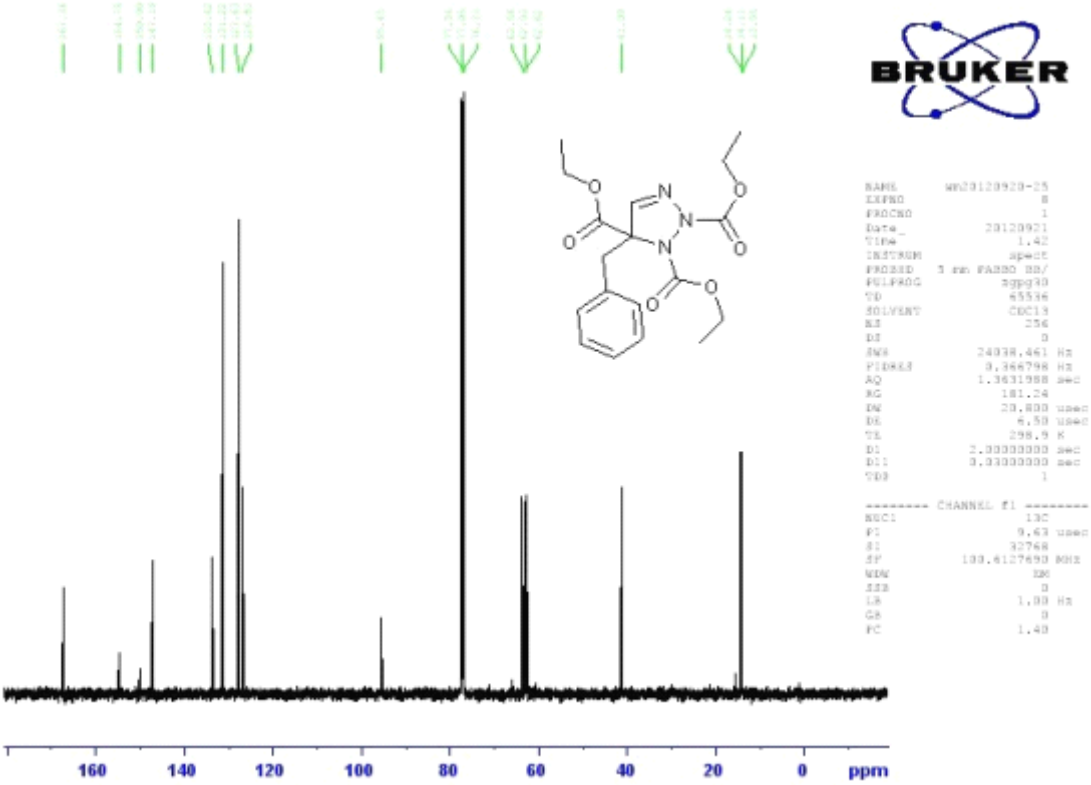
NMR for 3ba


7.310
7.137
7.123
7.118
7.108
7.100
4.227
4.209
4.201
4.183
4.165
4.154
4.136
4.127
4.109
4.004
3.986
3.977
3.959
3.941
3.933
3.915
3.906
3.889
3.733
3.441
3.405
3.339
3.304
1.240
1.222
1.204
1.101
1.084
1.066
0.000
BRUKER
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.97
4.34
2.06
2.06
3.00
1.02
1.00
3.05
2.90

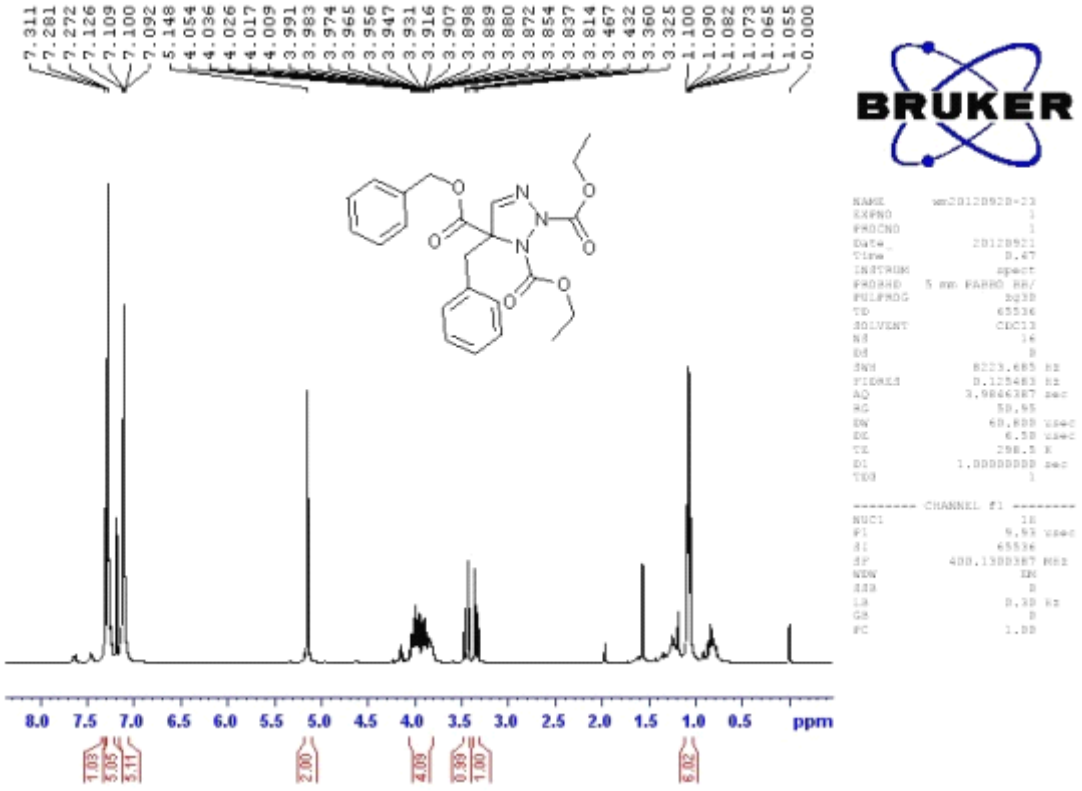

BRUKER
160 140 120 100 80 60 40 20 0 ppm

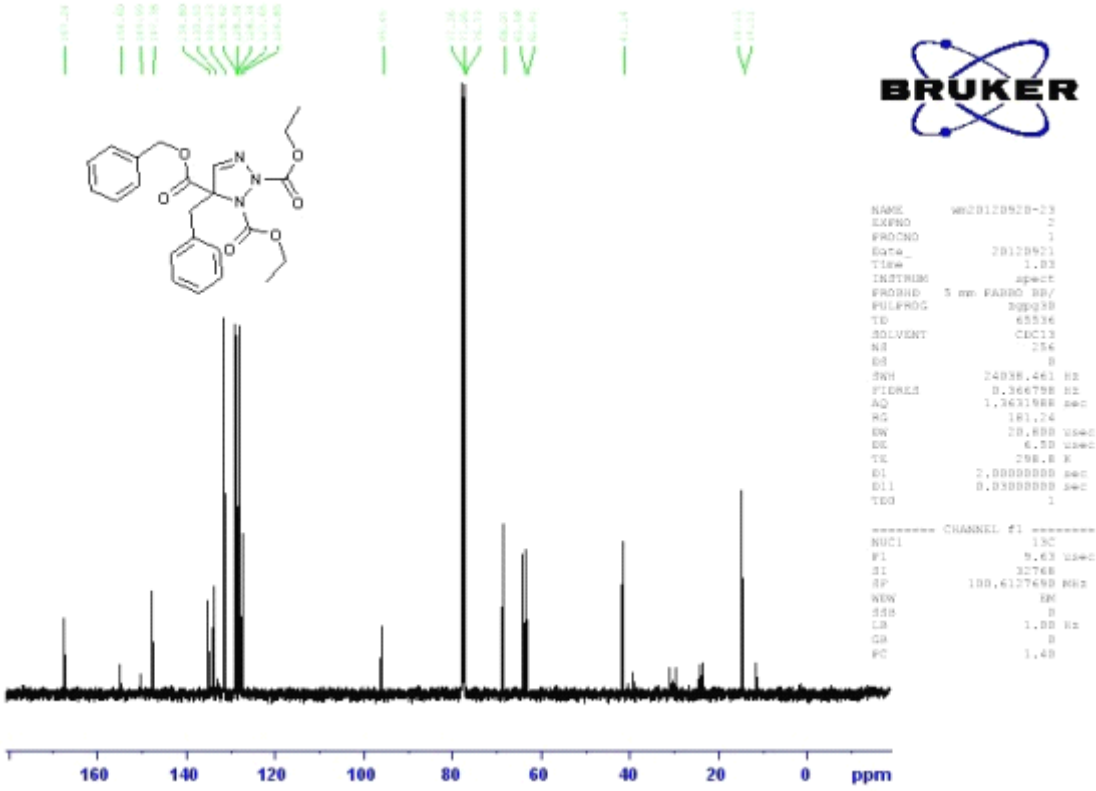
NMR for 3ca


7.309
7.133
7.118
7.107
4.229
4.220
4.211
4.202
4.192
4.184
4.166
4.158
4.147
4.140
4.123
4.114
4.096
4.004
3.995
3.986
3.978
3.960
3.949
3.942
3.932
3.914
3.905
3.887
3.444
3.409
3.337
3.302
1.243
1.225
1.208
1.103
1.086
1.068
BRUKER
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
5.00
4.04
2.70
1.07
0.99
6.08
3.07

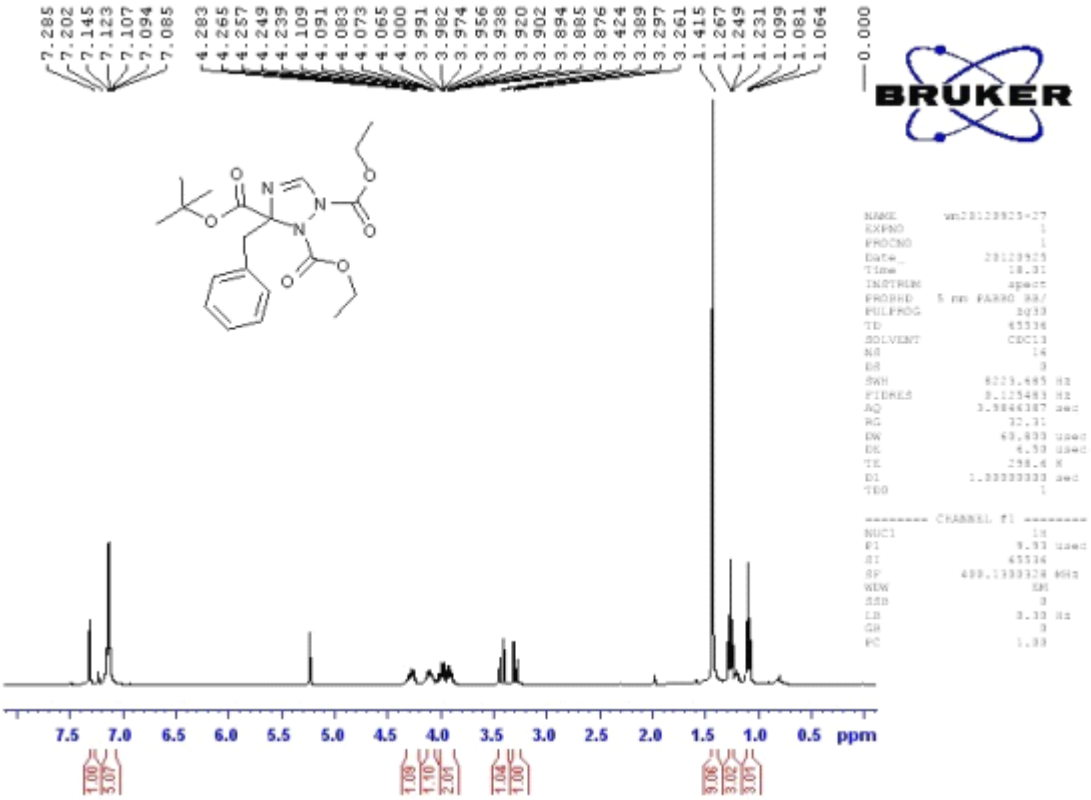

BRUKER
160 140 120 100 80 60 40 20 0 ppm

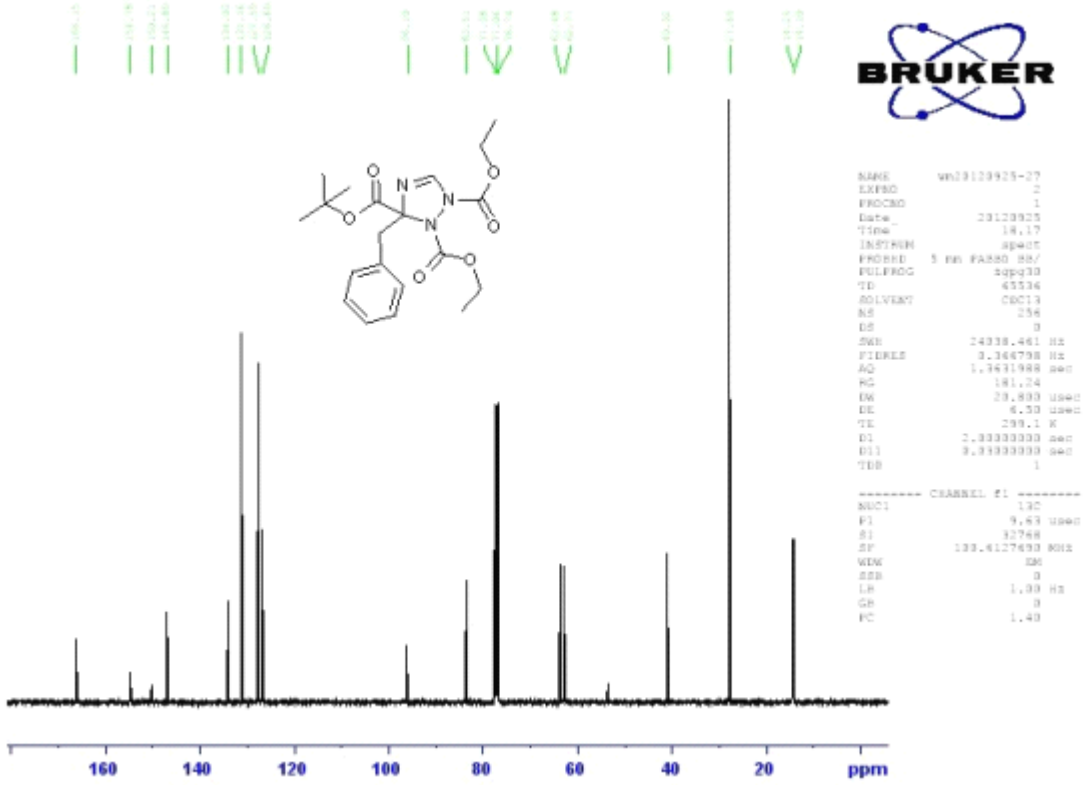
NMR for 3aa


7.311
7.281
7.272
7.126
7.109
7.100
7.092
5.148
4.054
4.036
4.026
4.017
4.009
3.991
3.983
3.974
3.965
3.956
3.947
3.931
3.916
3.907
3.898
3.889
3.880
3.872
3.854
3.837
3.814
3.467
3.432
3.360
3.325
1.100
1.090
1.082
1.073
1.065
1.055
0.000
BRUKER
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.03
3.05
5.11
2.00
4.05
0.99
1.00
6.02

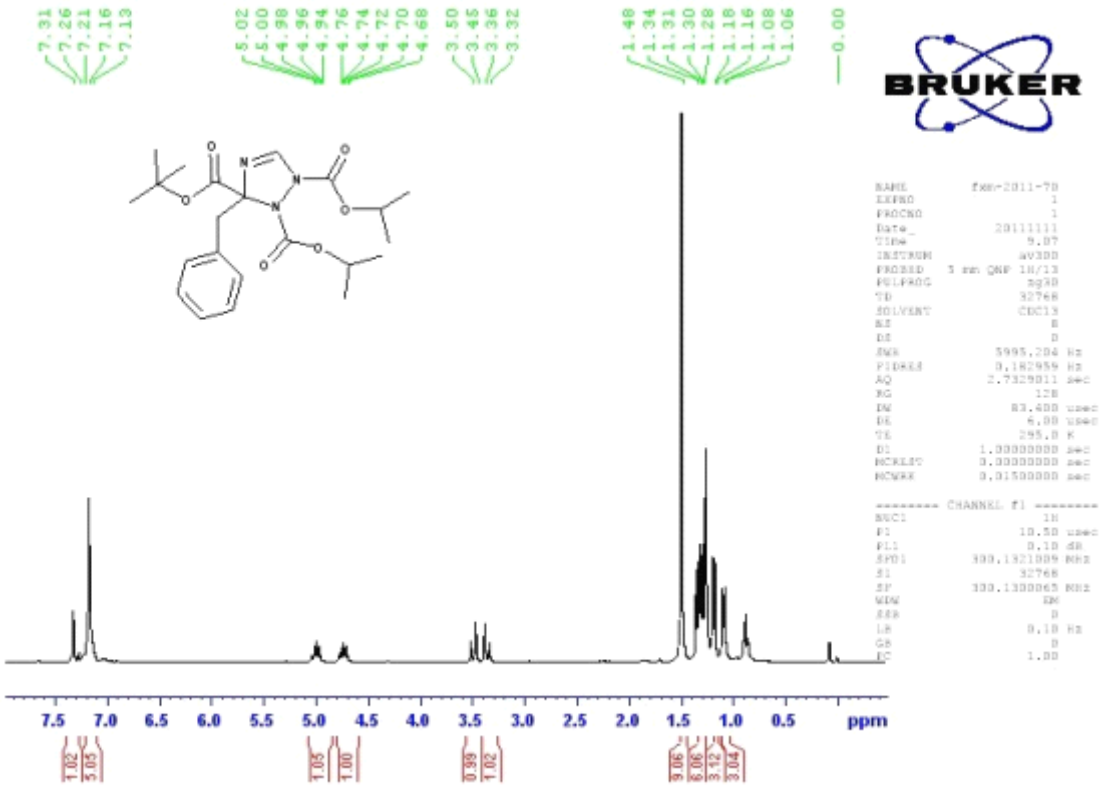

BRUKER
160 140 120 100 80 60 40 20 0 ppm

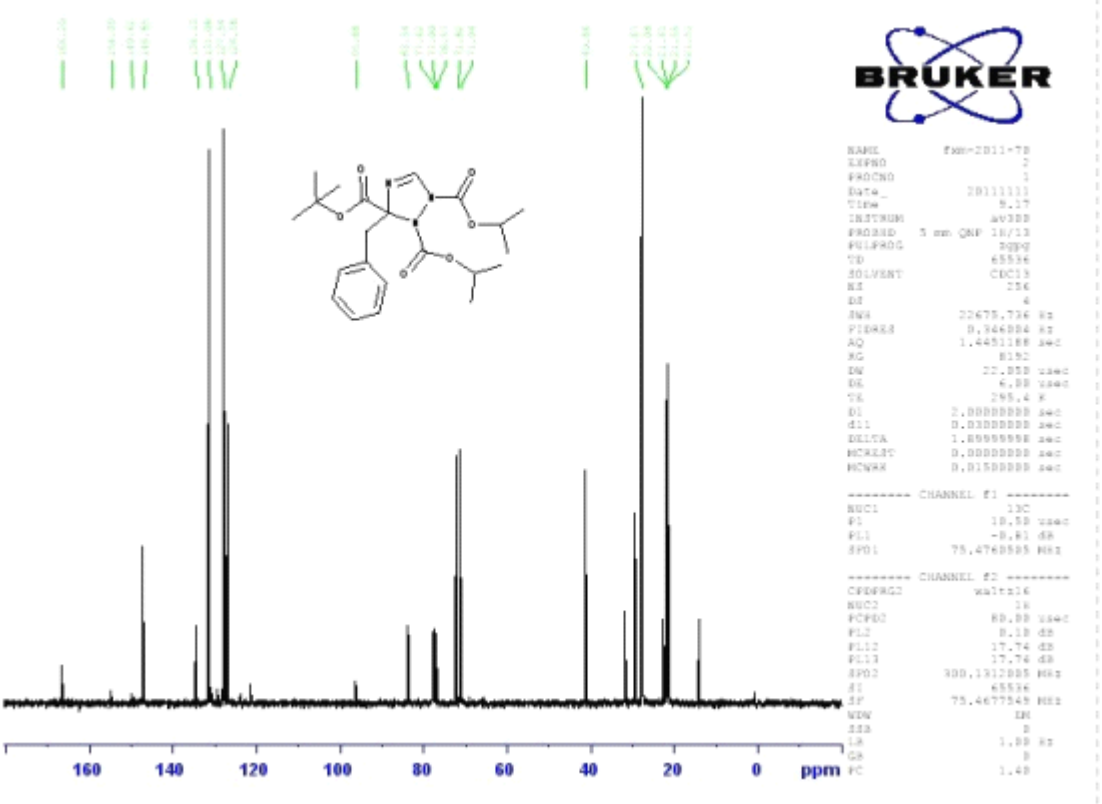
NMR for 3ka


7.285
7.202
7.145
7.123
7.107
7.094
7.085
4.283
4.265
4.257
4.249
4.239
4.109
4.091
4.083
4.073
4.065
4.000
3.991
3.982
3.974
3.956
3.938
3.920
3.902
3.894
3.885
3.876
3.424
3.389
3.297
3.261
1.415
1.267
1.249
1.231
1.099
1.081
1.064
0.000
BRUKER
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

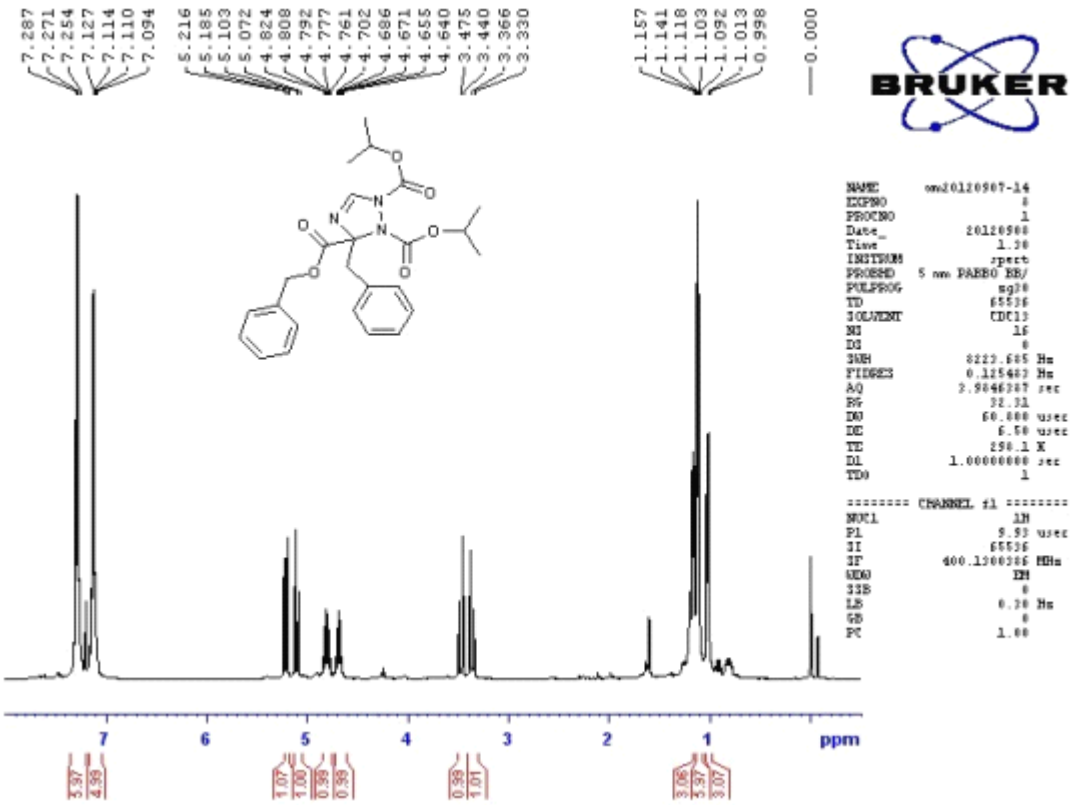

BRUKER
160 140 120 100 80 60 40 20 ppm

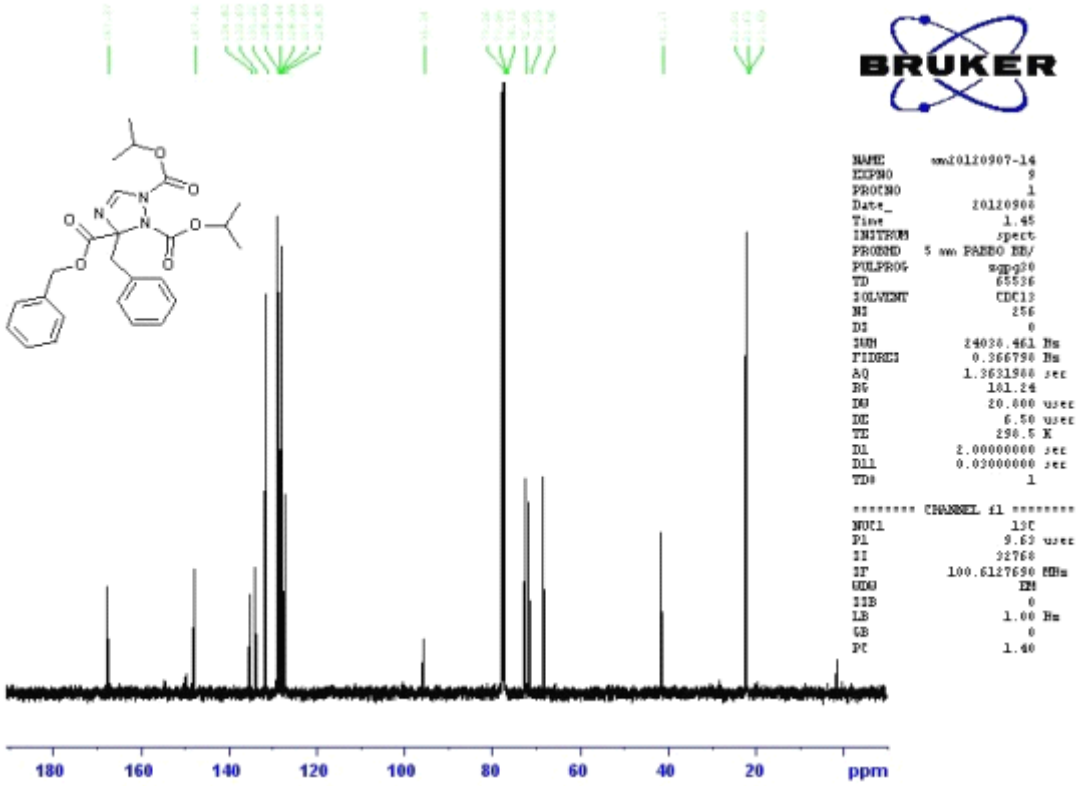
NMR for 3kb


7.31
7.26
7.21
7.16
7.13
5.02
5.00
4.98
4.96
4.94
4.76
4.74
4.72
4.70
4.68
3.50
3.45
3.36
3.32
1.48
1.34
1.31
1.30
1.28
1.18
1.16
1.08
1.06
0.00
BRUKER
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.02
3.05
1.05
1.00
0.99
1.02
9.06
6.06
3.12
3.04

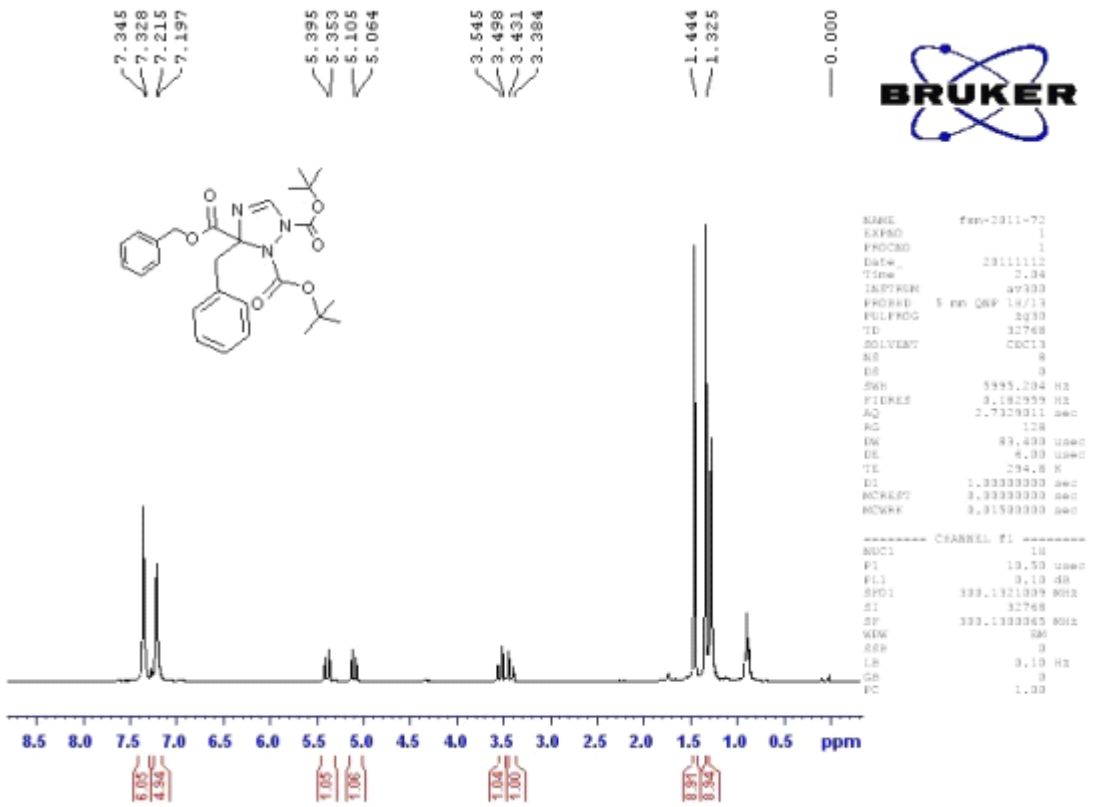

BRUKER
160
140
120
100
80
60
40
20
0
ppm

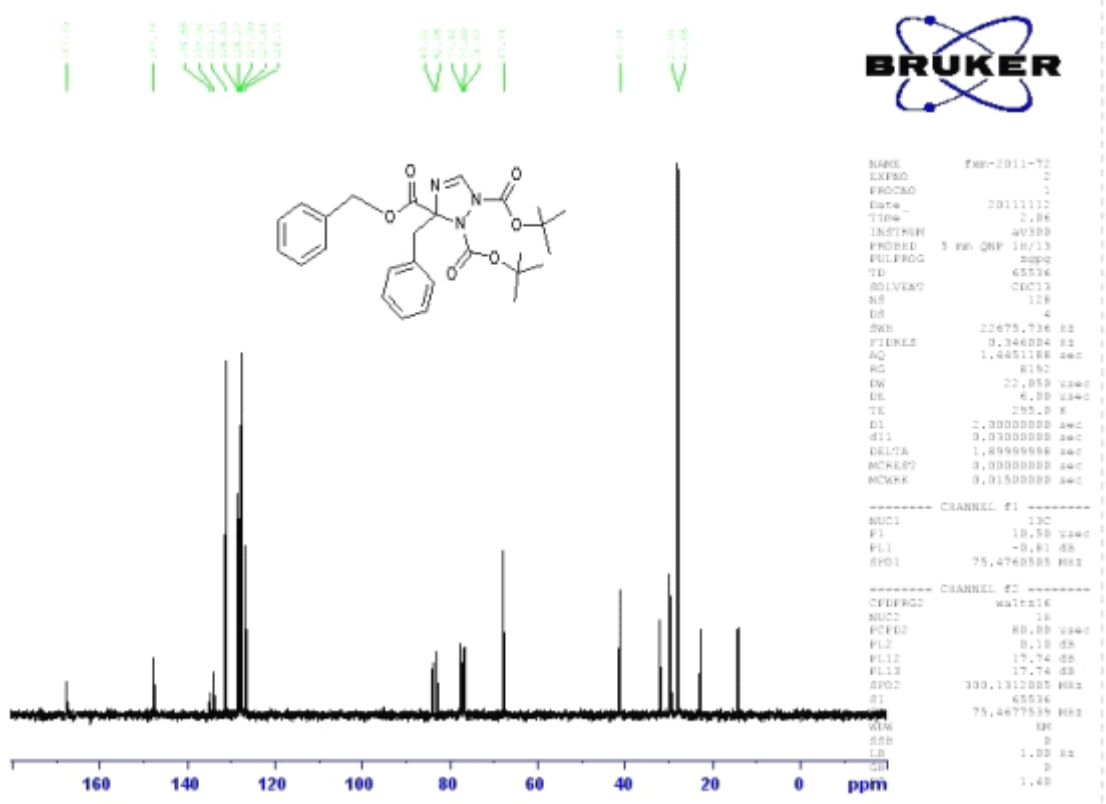
NMR for 3ab


7.287
7.271
7.254
7.127
7.114
7.110
7.094
5.216
5.185
5.103
5.072
4.824
4.808
4.792
4.777
4.761
4.702
4.686
4.671
4.655
4.640
3.475
3.440
3.366
3.330
1.157
1.141
1.118
1.103
1.092
1.013
0.998
0.000
BRUKER
7
6
5
4
3
2
1
ppm

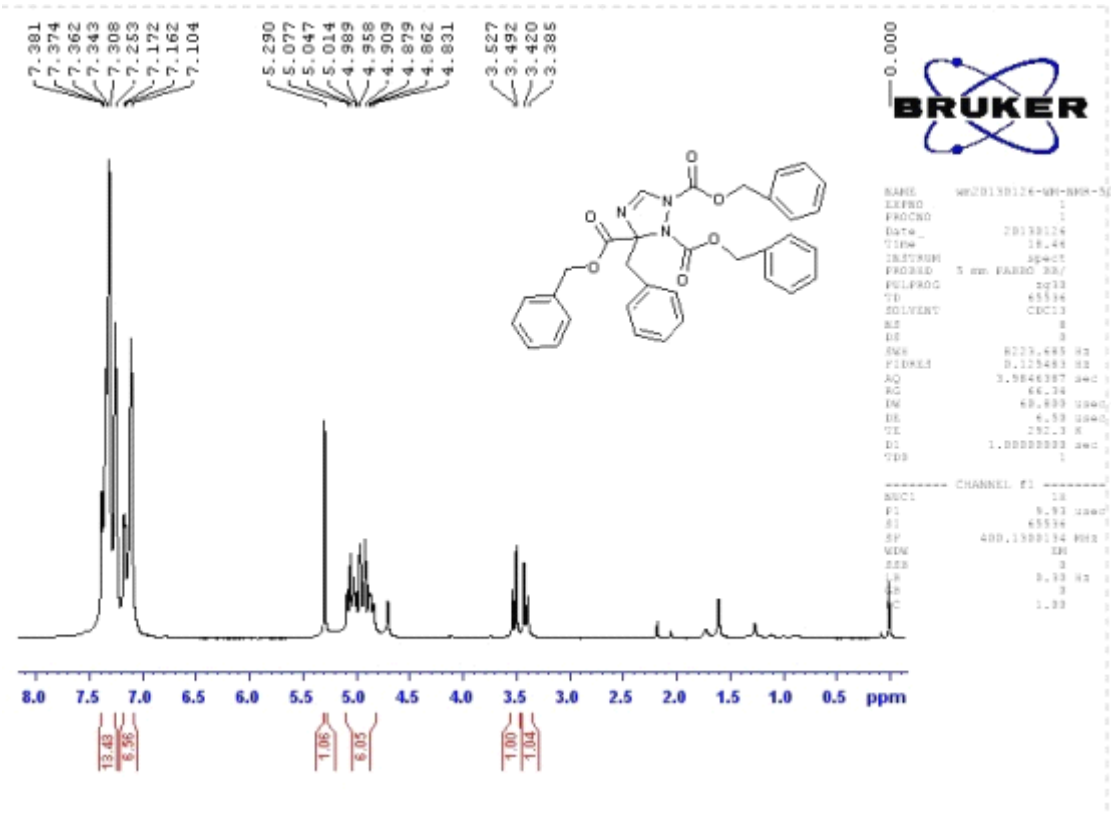

BRUKER
180
160
140
120
100
80
60
40
20
ppm

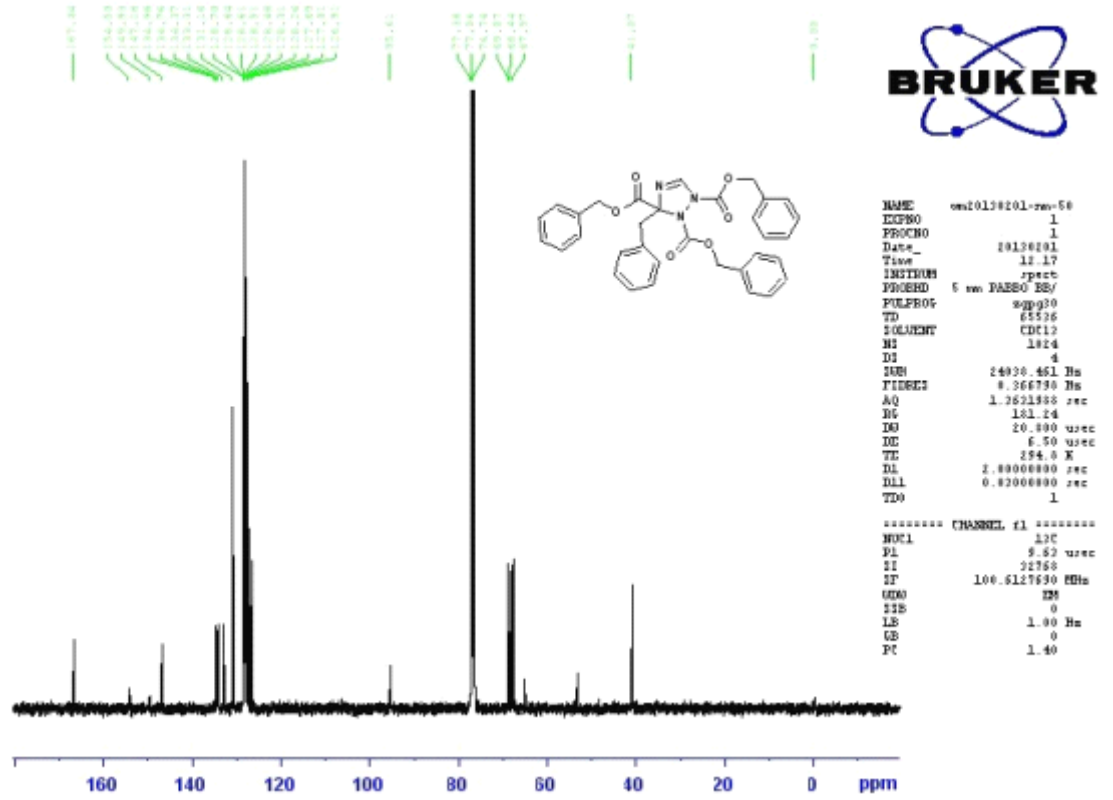
NMR for 3ac


7.345
7.328
7.215
7.197
5.395
5.353
5.105
5.064
3.545
3.498
3.431
3.384
1.444
1.325
0.000
BRUKER
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

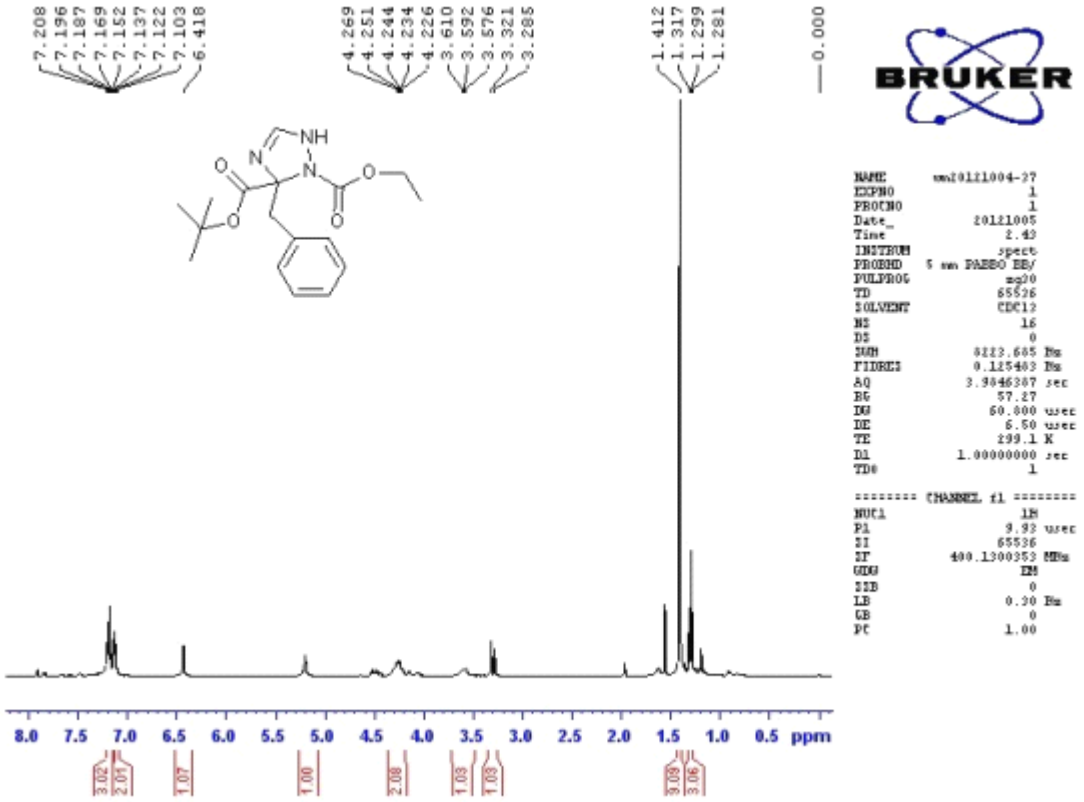

BRUKER
160 140 120 100 80 60 40 20 0 ppm

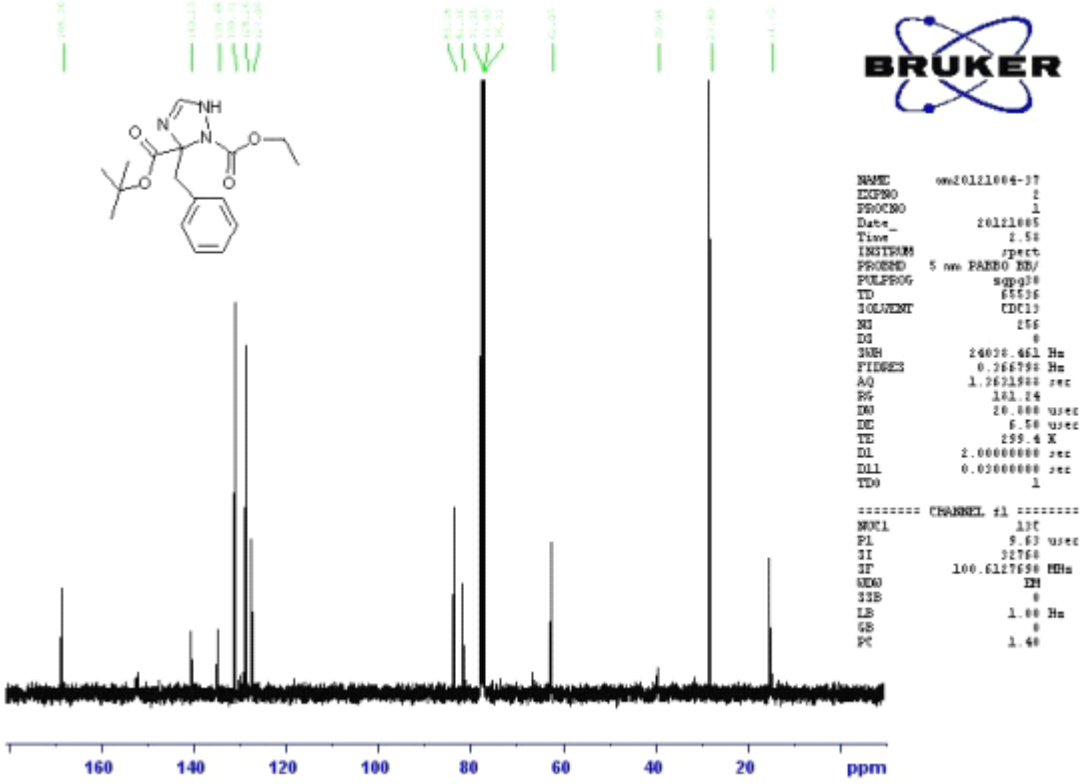
NMR for 3ad


7.381
7.374
7.362
7.343
7.308
7.253
7.172
7.162
7.104
5.290
5.077
5.047
5.014
4.989
4.958
4.909
4.879
4.862
4.831
3.527
3.492
3.420
3.385
0.000
BRUKER
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
13.43
6.56
1.06
6.05
1.00
1.04

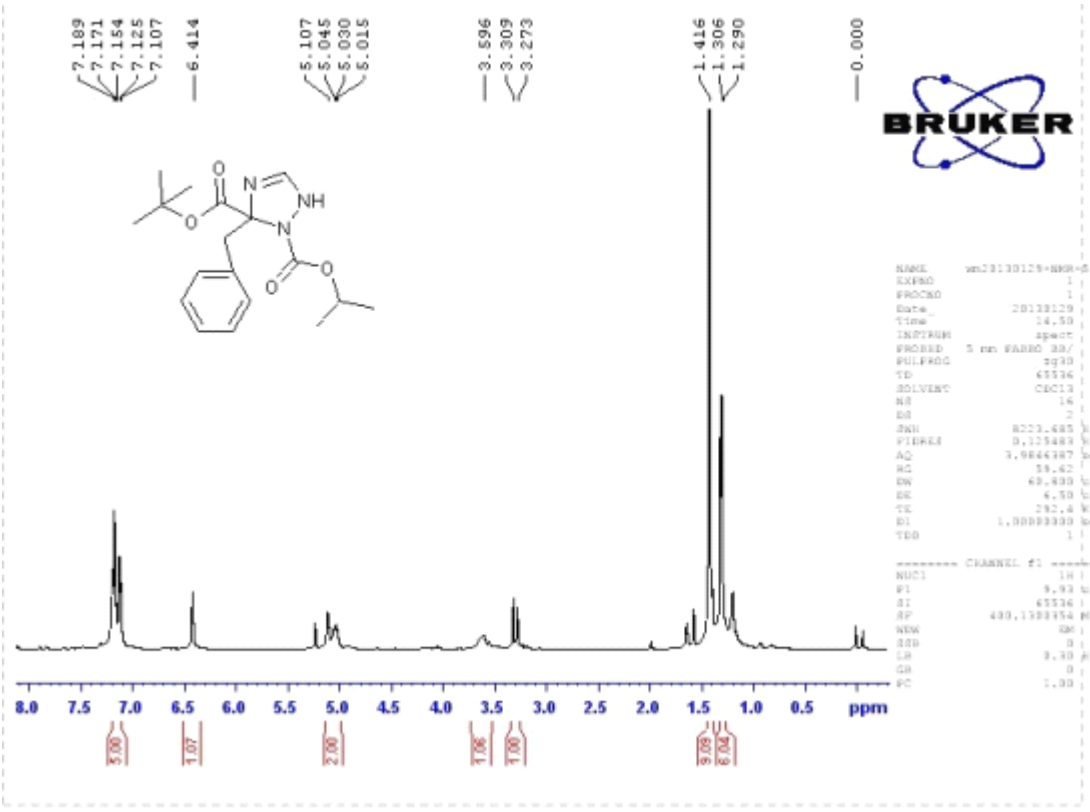

BRUKER
160 140 120 100 80 60 40 20 0 ppm

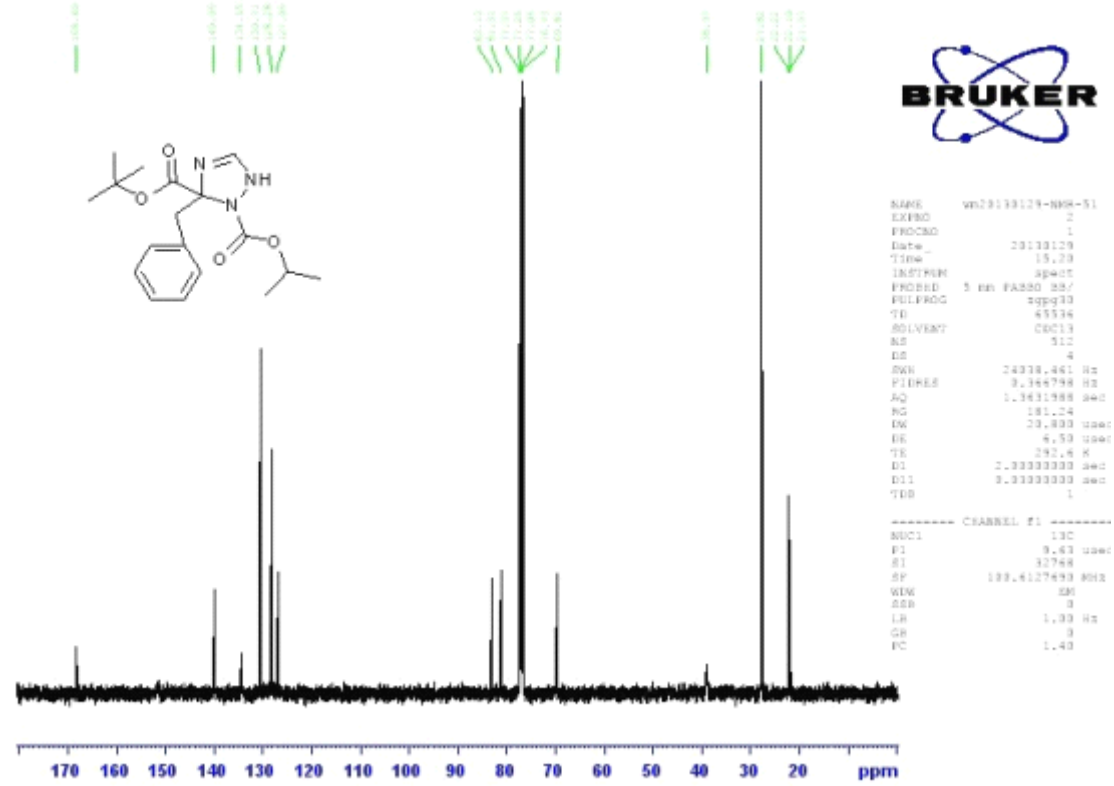
NMR for 4a


7.208
7.196
7.187
7.169
7.152
7.137
7.122
7.103
6.418
4.269
4.251
4.244
4.234
4.226
3.610
3.592
3.576
3.321
3.285
1.412
1.317
1.299
1.281
0.000
BRUKER
NAME
EXPNO
PROCNO
Date_
Time
INSTRUM
PROBHD
PULPROG
TD
SOLVENT
NS
DS
SWH
FIDRES
AQ
RG
DW
DE
TE
D1
TD0
CHANNEL f1
NUC1
P1
SI
SF
WDW
SSB
LB
GB
PC
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.02
2.01
1.07
1.00
2.08
1.03
1.03
3.09
3.06

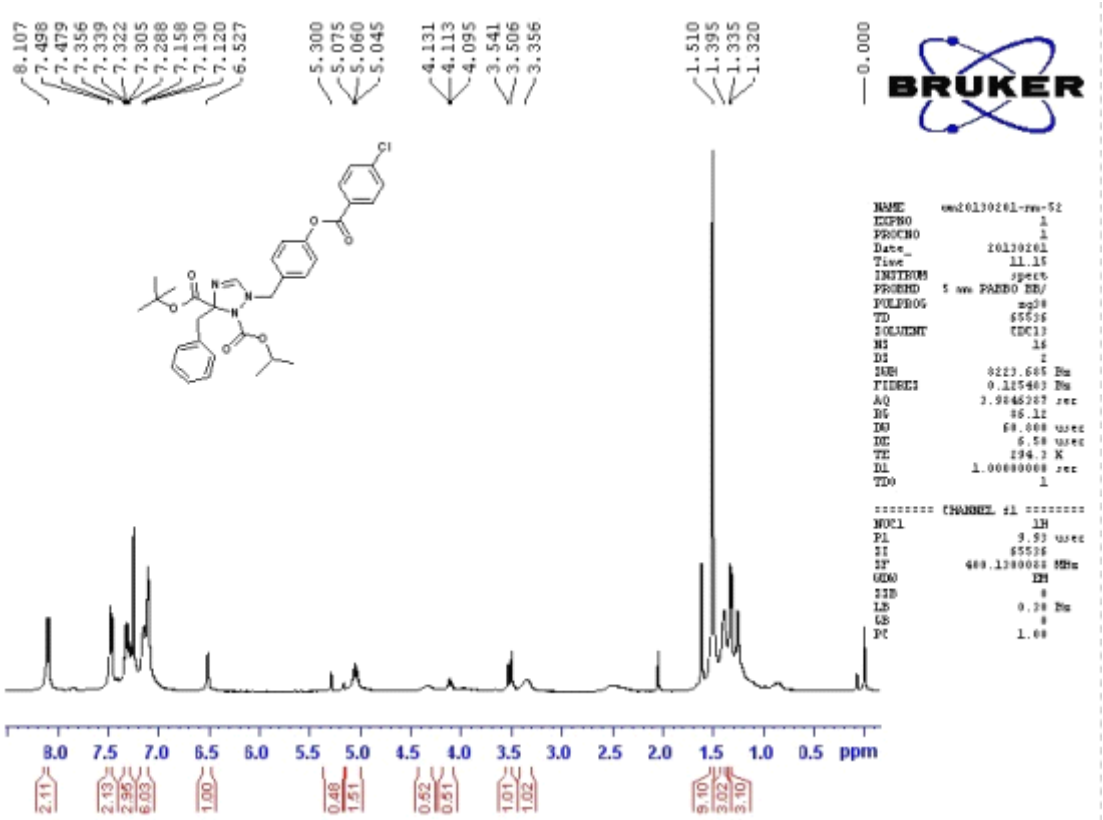

BRUKER
160 140 120 100 80 60 40 20 ppm

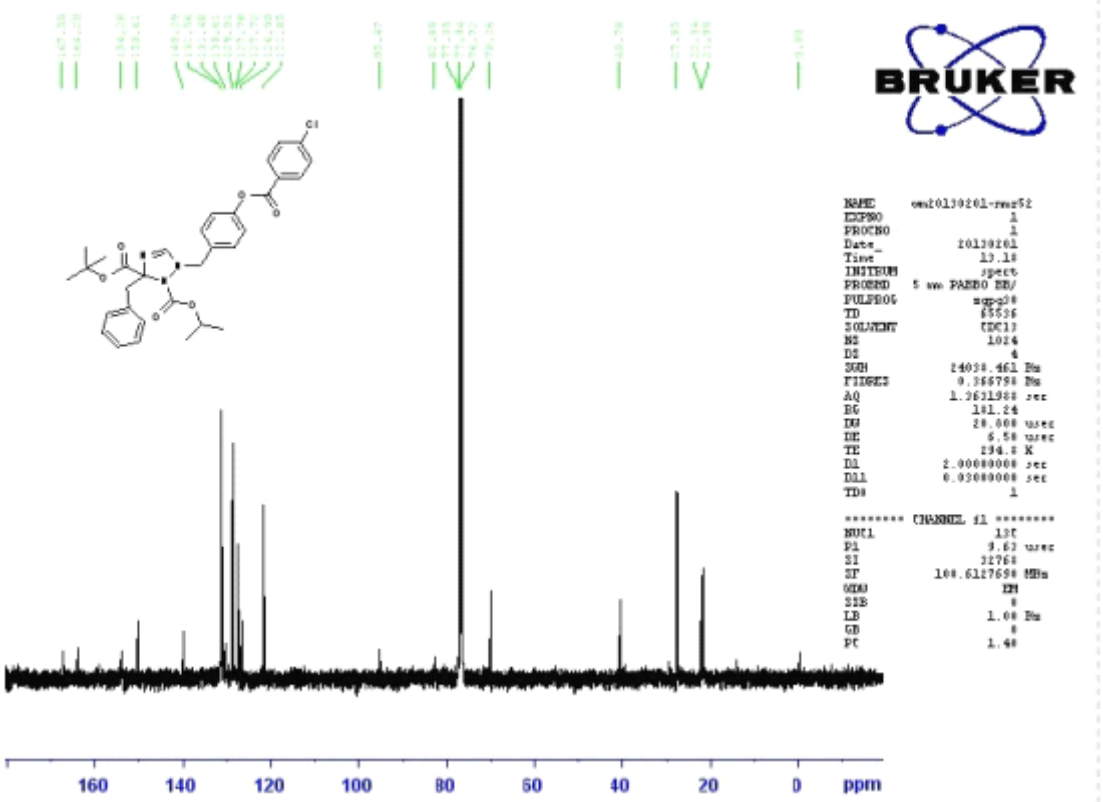
NMR for 4b


7.189
7.171
7.154
7.125
7.107
6.414
5.107
5.045
5.030
5.015
3.596
3.309
3.273
1.416
1.306
1.290
0.000
BRUKER
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.00
1.07
2.00
7.06
7.00
9.09
6.04

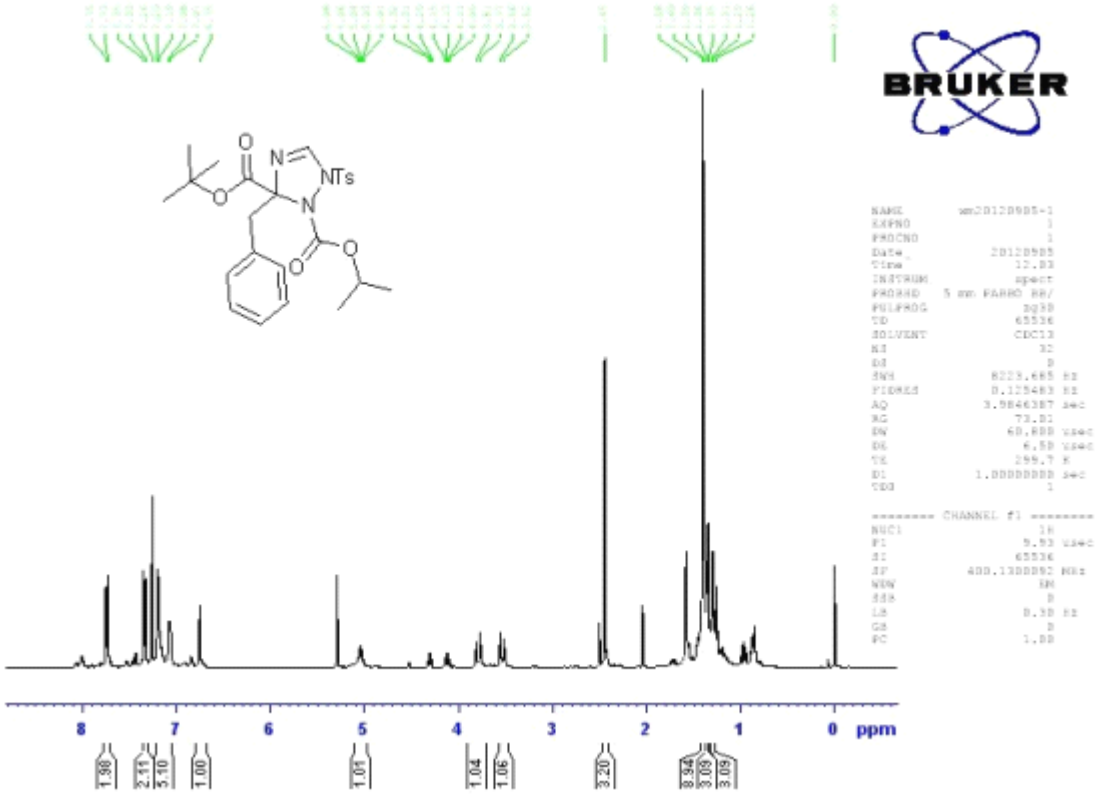

BRUKER
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

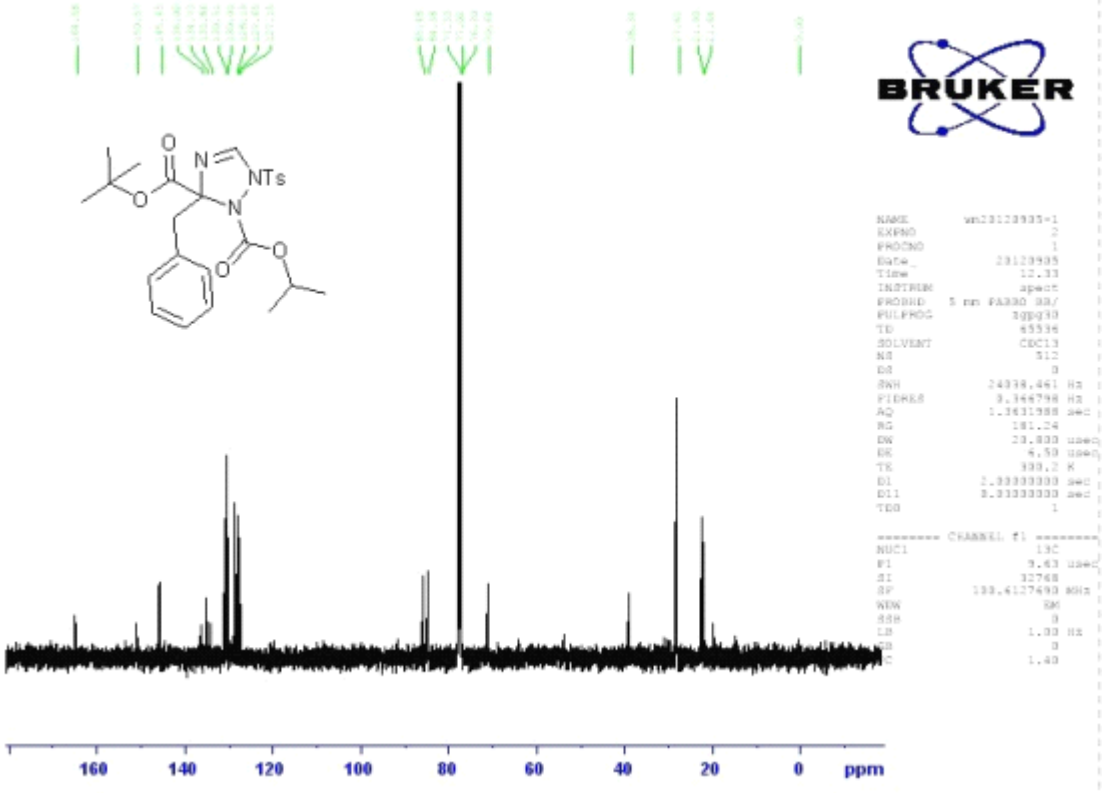
NMR for 5a


8.107
7.498
7.479
7.356
7.339
7.322
7.305
7.288
7.158
7.130
7.120
6.527
5.300
5.075
5.060
5.045
4.131
4.113
4.095
3.541
3.506
3.356
1.510
1.395
1.335
1.320
0.000
BRUKER
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.11
2.13
2.95
6.03
1.00
0.48
1.51
0.62
0.51
1.01
1.02
9.10
3.02
3.10


BRUKER
160 140 120 100 80 60 40 20 0 ppm

NMR for 5b


BRUKER
NTs
8
7
6
5
4
3
2
1
0
ppm
1.00
2.11
3.10
1.00
1.01
1.04
1.06
3.20
8.94
3.08
3.09


BRUKER
NTs
160
140
120
100
80
60
40
20
0
ppm

K. Reference

1. (*a*) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin, X. M. Feng, *Synlett*, 2005, 2445; (*b*) J. L. Huang, X. H. Liu, Y. H. Wen, B. Qin, X. M. Feng, *J. Org. Chem.*, 2007, **72**, 204; (*c*) J. L. Huang, J. Wang, X. H. Chen, Y. H. Wen, X. H. Liu, X. M. Feng, *Adv. Synth. Catal.*, 2008, **350**, 287; (*d*) X. Yang, X. Zhou, L. L. Lin, L. Chang, X. H. Liu, X. M. Feng, *Angew. Chem., Int. Ed.*, 2008, **47**, 7079; (*e*) D. J. Shang, J. G. Xin, Y. L. Liu, X. Zhou, X. H. Liu, X. M. Feng, *J. Org. Chem.*, 2008, **73**, 630; (*f*) D. J. Shang, Y. L. Liu, X. Zhou, X. H. Liu, X. M. Feng, *Chem. Eur. J.*, 2009, **15**, 3678; (*g*) Y. L. Liu, D. J. Shang, X. Zhou, X. H. Liu, X. M. Feng, *Chem. Eur. J.*, 2009, **15**, 2055.

2. (*a*) R. S. Hong, M. J. Bouma, R. F. Schmitz, F. Kanter, M. Lutz, A. L. Spek, R. Orru, *Org. Lett.*, 2003, **5**, 3759; (*b*) D. Monge, K. L. Jensen, I. Marı´n and K. A. Jørgensen, *Org. Lett.*, 2011, **32**, 328.

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