

**Chiral Cobalt(II) Complex Catalyzed Asymmetric Formal [3 + 2] Cycloaddition to
Synthesize 1,2,4-Triazolines**

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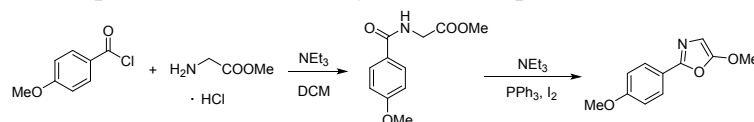
E-mail: xmfeng@scu.edu.cn

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(A) General information

Reactions were carried out using commercial available reagents in oven-dried apparatus. CH_2Cl_2 was dried over powdered CaH_2 and distilled under nitrogen. ^1H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. The preparation of 5-alkoxyoxazole compounds followed the literature.¹ Enantiomeric excesses were determined by HPLC analysis on Daicel Chiralcel IA, IB and IE in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^{25} = (c: \text{g}/100 \text{ mL}, \text{ in } \text{CH}_2\text{Cl}_2, \text{ D: } 589 \text{ nm})$. HRMS was recorded on a commercial apparatus (ESI Source, TOF).

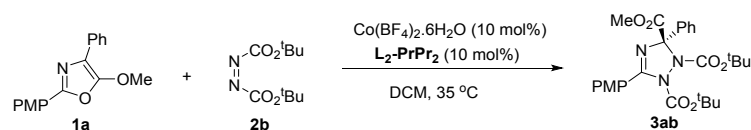
(B) Typical preparation procedure for 5-alkoxyoxazole compounds¹



The synthesis of all the 5-alkoxyoxazole compounds was according to the following preparation procedure. Add dropwise a solution of anisoyl chloride (3.41 g, 20 mmol) in CH_2Cl_2 (10 mL) to a suspension of glycine methyl ester hydrochloride (20 mmol) and triethylamine (4.83 mL, 44 mmol) in CH_2Cl_2 (30 mL) at 0 °C. After the reaction mixture was stirred at room temperature for 30 minutes, it was washed with aq. HCl (2 M, 20 mL), saturated aq. NaHCO_3 and saturated aq. NaCl, successively. Next the organic extract was dried (over NaSO_4) and concentrated under reduced pressure. Then the pure amide was obtained after recrystallization.

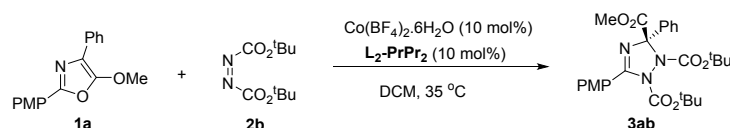
To a mixture of PPh_3 (2.62 g, 10 mmol) and I_2 (2.54 g, 10 mmol) in CH_2Cl_2 (25 mL) was added dropwise Et_3N (2.78 mL, 20 mmol) and stirred for 5–10 min. To this dark red solution was slowly added the amide (1.12 g, 5 mmol) in CH_2Cl_2 (15 mL) and the solution was stirred for 24 h. After concentration of the dark solution in vacuo, the residue was purified via flash silica gel column chromatography to get the 5-alkoxyoxazole compound.

(C) Typical procedure for asymmetric [3 + 2] reactions



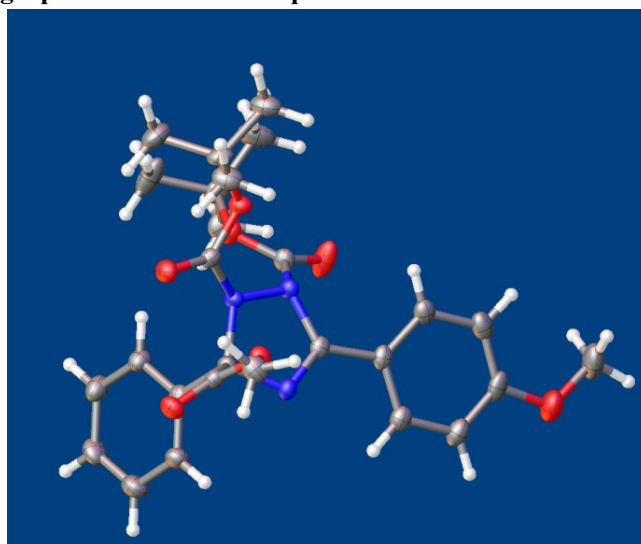
A dry reaction test tube was charged with $\text{L}_2\text{-PrPr}_2$ (10 mol%), $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mol%), and CH_2Cl_2 (1.0 mL), and the mixture was stirred at 35 °C for 0.5 h. Then, the 5-alkoxyoxazole **1a** (0.1 mmol) and the azodicarboxylate **2b** (0.12 mmol) were added. After being stirred at 35 °C for 24 h, the pure product was obtained by flash chromatography on silica gel (PE/EA = 5:1).

(D) Scaled-up version of the asymmetric reaction



A dry reaction flask was charged with **L₂-PrPr₂** (10 mol%), Co(BF₄)₂·6H₂O (10 mol%) and THF (5.0 mL). After stirring at 35 °C for 0.5 h, the solvent was evaporated in vacuo. Next, the 5-alkoxyoxazole **1a** (3.0 mmol) and the azodicarboxylate **2b** (3.6 mmol) were added to the reaction flask, following the addition of DCM (30 mL). After being stirred at 35 °C for 24 h, the solvent was removed and the pure product **3ab** was obtained by flash chromatography on silica gel (PE/EA = 5:1).

(E) X-ray crystallographic structure of the product **3ab**



Single crystal of **3ab** [C₂₇H₃₃N₃O₇] was obtained from the mixed solvents of ethyl acetate and petroleum ether. CCDC 1531931 containing the supplementary crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

(F) Optimization of the reaction conditions

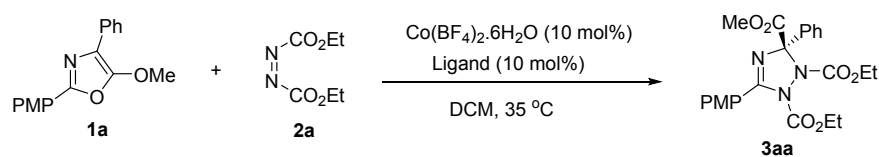
Table 1: Screening of the metal salts for the reaction of diethyl-diazene-1,2-dicarboxylate **2a**^[a]

Entry	Metal salt	Yield (%) ^[b]	Ee (%) ^[c]
1	Cu(OTf) ₂	60	0
2	Mg(OTf) ₂	99	4
3	Zn(OTf) ₂	93	49
4	Sc(OTf) ₃	77	3
5	Ni(OTf) ₂	99	48
6	Yb(OTf) ₃	88	13
7	Bi(OTf) ₃	71	0
8	Ga(OTf) ₃	87	0
9	Y(OTf) ₃	90	7
10	La(OTf) ₃	85	37

11	Fe(OTf) ₃	71	0
12	Zn(NTf ₂) ₂	97	35
13	Ni(BF ₄) ₂ ·6H ₂ O	99	0
14	Co(BF ₄) ₂ ·6H ₂ O	97	72

[a] Unless otherwise noted, the reaction was performed with metal salt (10 mol%), **L-PrPr₂** (10 mol%) and **2a** (1.2 equiv) in CH₂Cl₂ (1.0 mL) at 35 °C for 0.5 h, then **1a** (0.1 mmol) was added, the reaction mixture was stirred for 20 h. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase (Chiralpak IB).

Table 2: Screening of the chiral ligands for the reaction of diethyl-diazene-1,2-dicarboxylate **2a** [a]



Entry	Ligand	Yield (%) ^[b]	Ee (%) ^[c]
1	L-PiPr₂	98	64
2	L-RaPr₂	89	65
3	L-ProPh	73	69
4	L-PrPr₃	84	70
5	L-Pro^tBu	88	76
6	L-PrMe₂	99	0
7	L-PrmMe₂	95	4
8	L-ProOMe	52	66
9	L-PrEt₂	98	52
10	L-PrPh	83	0
11	L-PrpBr	99	0

[a] Unless otherwise noted, the reaction was performed with Co(BF₄)₂·6H₂O (10 mol%), the ligand (10 mol%) and **2a** (1.2 equiv) in CH₂Cl₂ (1.0 mL) at 35 °C for 0.5 h, then **1a** (0.1 mmol) was added, the reaction mixture was stirred for 20 h. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase (Chiralpak IB).

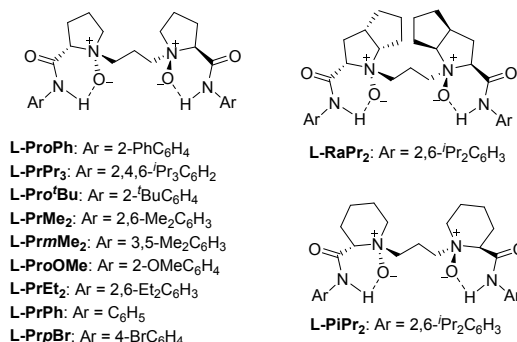
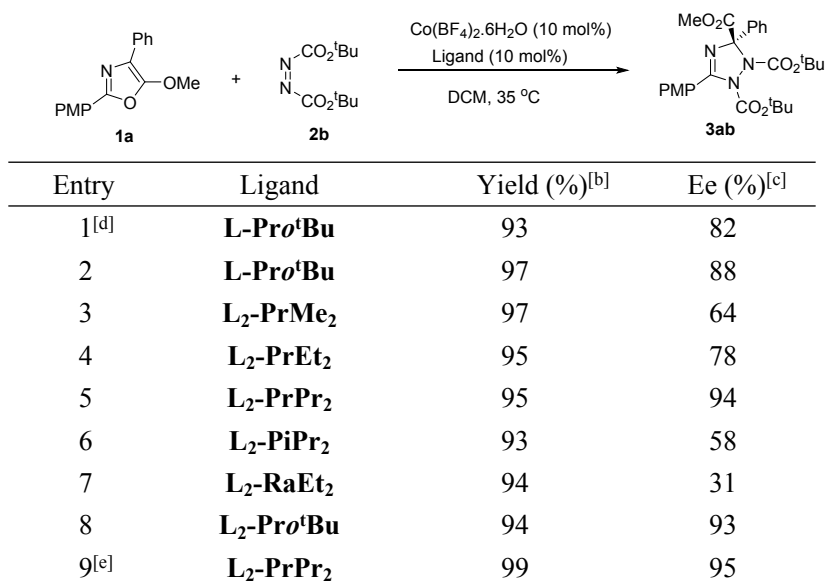


Table 3: Screening of the ligands for the reaction of diazene-1,2-dicarboxylate **2b** [a]



[a] Unless otherwise noted, the reaction was performed with Co(BF₄)₂·6H₂O (10 mol%) and the ligand (10 mol%) in CH₂Cl₂ (1.0 mL) at 35 °C for 0.5 h, then **1a** (0.1 mmol) and **2b** (1.2 equiv) was added, the reaction mixture was stirred for 20 h. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase (Chiralpak IA). [d] The reaction was performed with Co(BF₄)₂·6H₂O (10 mol%), **L-Pro^tBu** (10 mol%) and **2b** (1.2 equiv) in CH₂Cl₂ (1.0 mL) at 35 °C for 0.5 h, then **1a** (0.1 mmol) was added, then stirring for 20 h. [e] The reaction was performed for 24 h.

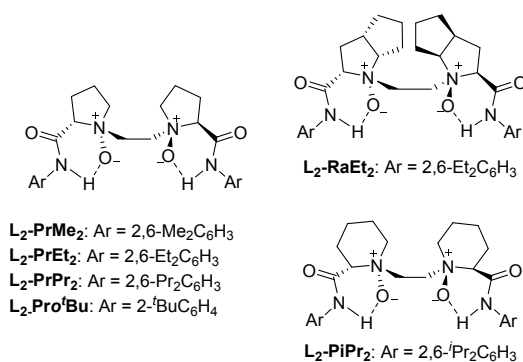
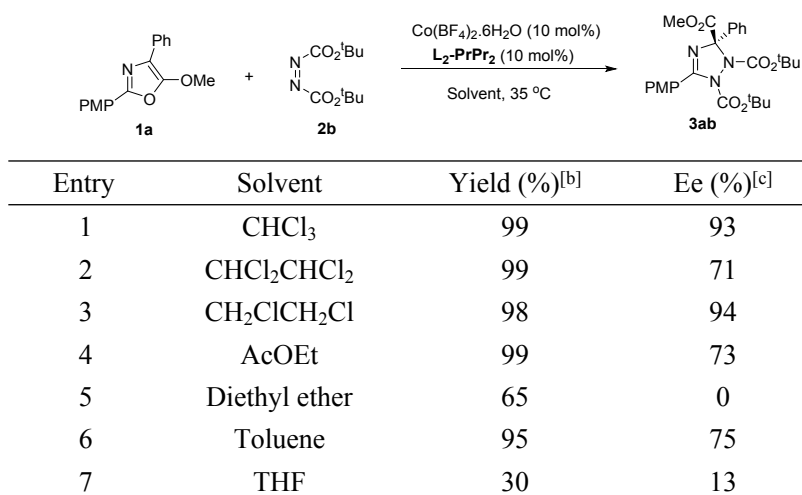
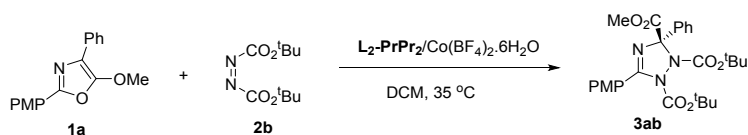


Table 4: Screening of the reaction solvent ^[a]



[a] Unless otherwise noted, the reaction was performed with **L₂-PrPr₂** (10 mol%) and Co(BF₄)₂·6H₂O (10 mol%) in solvent (1.0 mL) at 35 °C for 0.5 h, then **1a** (0.1 mmol) and **2b** (1.2 equiv) was added, the reaction mixture was stirred for 24 h. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase (Chiralpak IA).

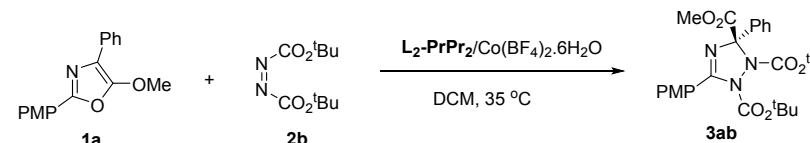
Table 5: Screening of the ratio of **L₂-PrPr₂** and Co(BF₄)₂·6H₂O [a]



Entry	L₂-PrPr₂ : Co(BF ₄) ₂ ·6H ₂ O	Yield (%) ^[b]	Ee (%) ^[c]
1	1:1	99	95
2	1.1:1	97	93
3	1.2:1	99	88
4	1:1.1	99	92
5 ^[d]	1:1	75	91

[a] Unless otherwise noted, the reaction was performed with 10 mol% of **L₂-PrPr₂**/Co(BF₄)₂·6H₂O in CH₂Cl₂ (1.0 mL) at 35 °C for 0.5 h, then **1a** (0.1 mmol) and **2b** (1.2 equiv) was added, the reaction mixture was stirred for 24 h. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase (Chiralpak IA). [d] The reaction was performed with **L₂-PrPr₂** (5 mol%) and Co(BF₄)₂·6H₂O (5 mol%).

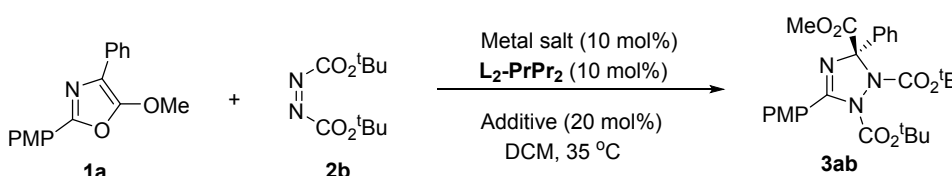
Table 6: Screening of the ratio of **1a/2b** [a]



Entry	1a/2b	Yield (%) ^[b]	Ee (%) ^[c]
1	1:1.2	99	95
2	1:1.1	97	93
3	1:1	92	92
4	1.2:1	99	92

[a] Unless otherwise noted, the reaction was performed with 10 mol% of **L₂-PrPr₂**/Co(BF₄)₂·6H₂O in CH₂Cl₂ (1.0 mL) at 35 °C for 0.5 h, then **1a** and **2b** was added, the reaction mixture was stirred for 24 h. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase (Chiralpak IA).

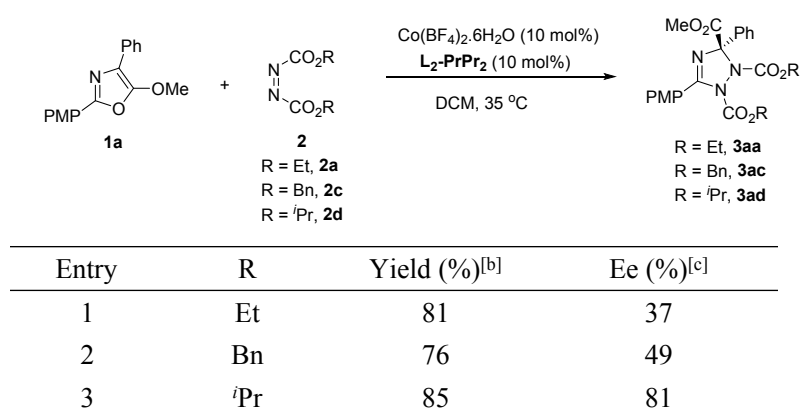
Table 7: Screening of the counterion of the metal salt and additive [a]



Entry	Metal salt	Additive	Yield (%) ^[b]	Ee (%) ^[c]
1	Co(ClO ₄) ₂ ·6H ₂ O		93	90
2	Co(acac) ₂		86	0
3	CoBr ₂		90	21
4	Co(BF ₄) ₂ ·6H ₂ O	NaBAR ₄ ^F	39	60
5	Co(BF ₄) ₂ ·6H ₂ O	LiNTf ₂	87	83

[a] Unless otherwise noted, the reaction was performed with **L₂-PrPr₂** (10 mol%), metal salt (10 mol%) and the additive (20 mol%) in CH₂Cl₂ (1.0 mL) at 35 °C for 0.5 h, then **1a** (0.1 mmol) and **2b** (1.2 equiv) was added, the reaction mixture was stirred for 24 h. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase (Chiralpak IA).

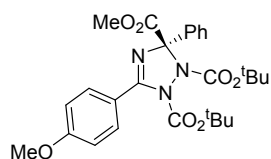
Table 8: The effect of the ester group of azodicarboxylates on the reaction ^[a]



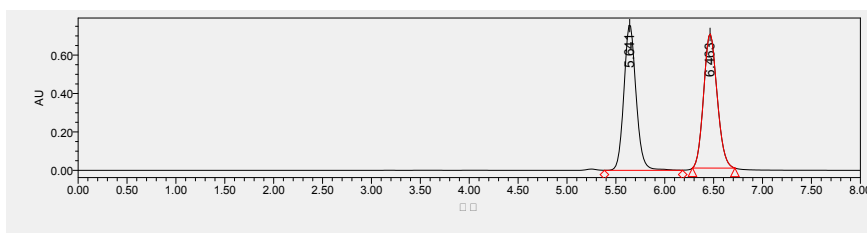
[a] Unless otherwise noted, the reaction was performed with **L₂-PrPr₂** (10 mol%), Co(BF₄)₂·6H₂O (10 mol%) in CH₂Cl₂ (1.0 mL) at 35 °C for 0.5 h, then **1a** (0.1 mmol) and **2** (1.2 equiv) was added, the reaction mixture was stirred for 24 h. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase (Chiralpak IB).

(G) Spectral characterization data for the products

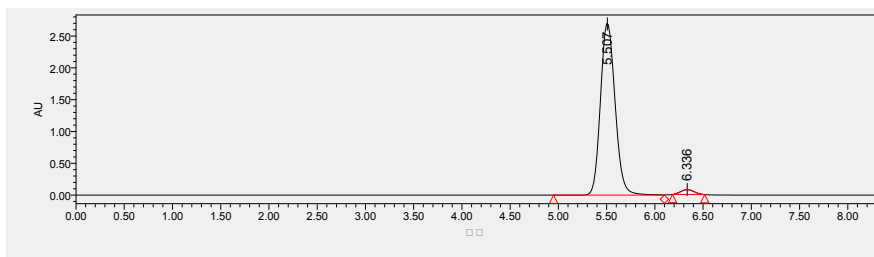
1,2-di-tert-butyl 3-methyl (R)-5-(4-methoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3ab**)



White solid; 99% yield, 95% ee; $[\alpha]^{14.0}_D = +69.8$ (c 1.01, CH₂Cl₂); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), *t* (major) = 5.51 min, *t* (minor) = 6.34 min; ¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.82 (m, 2H), 7.70 – 7.68 (m, 2H), 7.42 – 7.33 (m, 3H), 6.94 – 6.91 (m, 2H), 3.84 (s, 3H), 3.74 (s, 3H), 1.54 (s, 9H), 1.31 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 162.4, 158.8, 153.2, 151.2, 137.8, 132.0, 128.5, 127.8, 127.3, 121.1, 113.2, 93.0, 84.0, 82.7, 55.4, 53.2, 28.1, 27.7; HRMS (ESI-TOF): Calcd for C₂₇H₃₃N₃O₇Na⁺[M+Na]⁺ 534.2216, Found 534.2224.

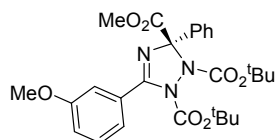


Entry	Retention Time	Area	% Area
1	5.641	6583150	49.53
2	6.463	6707466	50.47

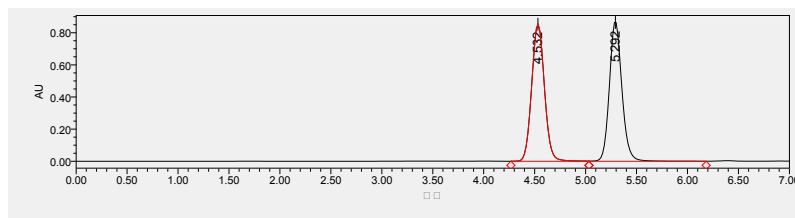


Entry	Retention Time	Area	% Area
1	5.507	28433975	97.43
2	6.336	750078	2.57

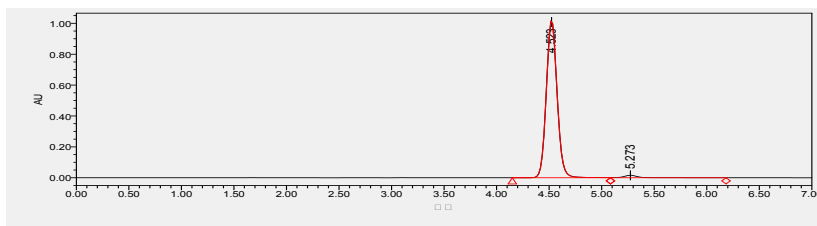
1,2-di-tert-butyl 3-methyl (R)-5-(3-methoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3bb**)



Colorless oil; 99% yield, 96% ee; $[\alpha]^{14.0}_D = +37.1$ (c 1.01, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 4.52 min, t (minor) = 5.27 min; ^1H NMR (400 MHz, CDCl_3) δ 7.72 – 7.69 (m, 2H), 7.46 – 7.41 (m, 3H), 7.39 – 7.35 (m, 2H), 7.33 (t, $J = 7.9$ Hz, 1H), 7.05 – 7.02 (m, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 1.54 (s, 9H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.2, 159.1, 159.0, 153.3, 150.9, 137.5, 130.2, 128.9, 128.5, 127.9, 127.3, 122.6, 117.8, 114.7, 93.4, 84.1, 82.9, 55.4, 53.2, 28.1, 27.6; HRMS (ESI-TOF): Calcd for $\text{C}_{27}\text{H}_{33}\text{N}_3\text{O}_7\text{Na}^+[\text{M}+\text{Na}]^+$ 534.2216, Found 534.2223.

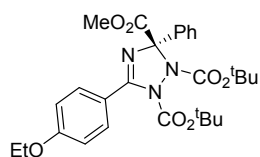


Entry	Retention Time	Area	% Area
1	4.532	7430721	50.03
2	5.292	7422575	49.97

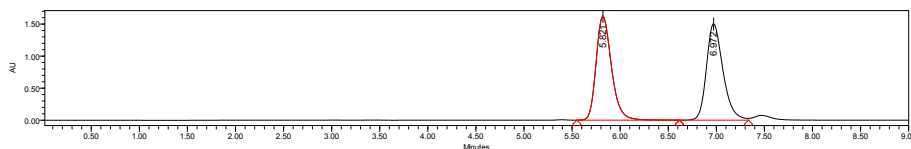


Entry	Retention Time	Area	% Area
1	4.523	7294032	97.98
2	5.273	150456	2.02

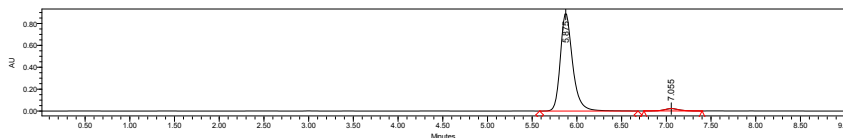
1,2-di-tert-butyl 3-methyl (R)-5-(4-ethoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3cb**)



Colorless oil; 99% yield, 94% ee; $[\alpha]^{14.1}_D = +75.2$ (c 1.02, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), *t* (major) = 5.86 min, *t* (minor) = 7.06 min; ^1H NMR (400 MHz, CDCl_3) δ 7.84 – 7.81 (m, 2H), 7.71 – 7.68 (m, 2H), 7.42 – 7.33 (m, 3H), 6.92 – 6.89 (m, 2H), 4.08 (t, $J = 7.0$ Hz, 2H), 3.74 (s, 3H), 1.54 (s, 9H), 1.42 (t, $J = 7.2$ Hz, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.4, 161.9, 158.8, 153.2, 151.2, 137.8, 132.0, 128.4, 127.8, 127.3, 120.9, 113.7, 92.9, 84.0, 82.7, 63.6, 53.2, 28.1, 27.7, 14.7; HRMS (ESI-TOF): Calcd for $\text{C}_{28}\text{H}_{35}\text{N}_3\text{O}_7\text{Na}^+[\text{M}+\text{Na}]^+$ 548.2373, Found 548.2366.

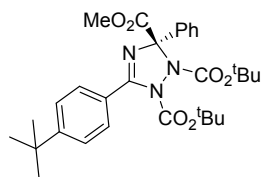


Entry	Retention Time	Area	% Area
1	5.821	18027125	50.06
2	6.972	17983264	49.94

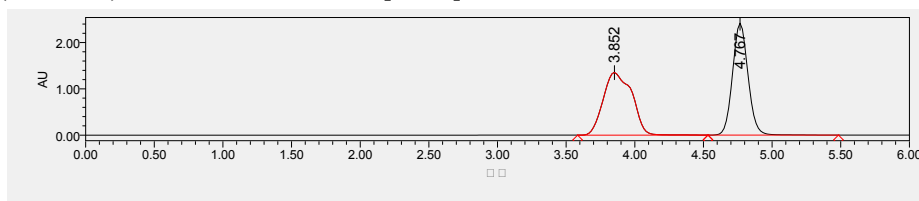


Entry	Retention Time	Area	% Area
1	5.875	8518274	97.21
2	7.055	244505	2.79

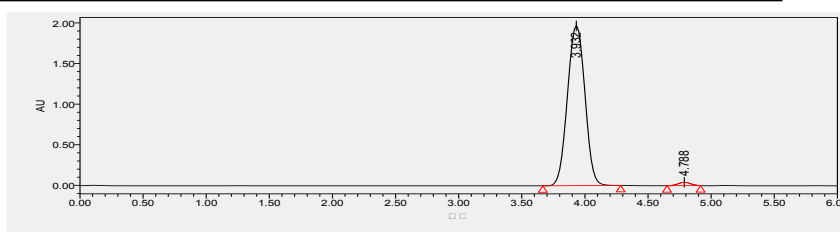
1,2-di-tert-butyl 3-methyl (R)-5-(4-(tert-butyl)phenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3db**)



Colorless oil; 99% yield, 97% ee; $[\alpha]^{14.1}_D = +55.7$ (c 1.14, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 3.93 min, t (minor) = 4.79 min; ^1H NMR (400 MHz, CDCl_3) δ 7.82 – 7.79 (m, 2H), 7.72 – 7.70 (m, 2H), 7.45 – 7.42 (m, 2H), 7.41 – 7.39 (m, 2H), 7.38 – 7.33 (m, 1H), 3.74 (s, 3H), 1.54 (s, 9H), 1.33 (s, 9H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 159.1, 155.2, 153.3, 151.1, 137.7, 129.8, 128.5, 127.9, 127.3, 126.1, 124.8, 93.1, 84.0, 82.8, 53.2, 35.0, 31.1, 28.1, 27.6; HRMS (ESI-TOF): Calcd for $\text{C}_{30}\text{H}_{40}\text{N}_3\text{O}_6[\text{M}+\text{H}]^+$ 538.2917, Found 538.2920.

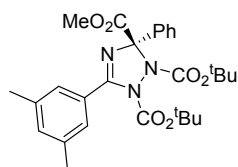


Entry	Retention Time	Area	% Area
1	3.852	19626316	50.81
2	4.767	19001762	49.19



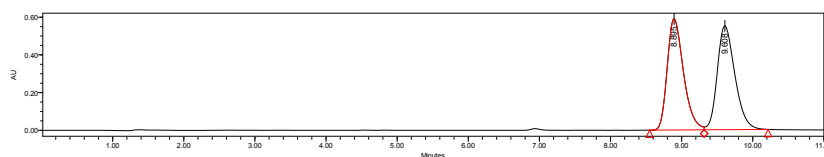
Entry	Retention Time	Area	% Area
1	3.932	18939234	98.51
2	4.788	287342	1.49

1,2-di-tert-butyl 3-methyl (R)-5-(3,5-dimethylphenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(H)-tricarboxylate (**3eb**)

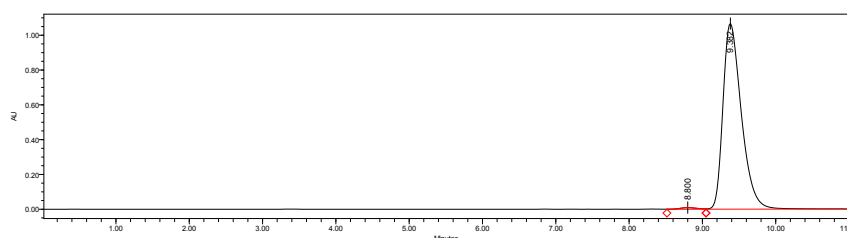


Colorless oil; 99% yield, 98% ee; $[\alpha]^{14.1}_D = +22.6$ (c 0.99, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 20/80, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 9.38 min, t (minor) = 8.80 min; ^1H NMR (400 MHz, CDCl_3) δ 7.72 – 7.70 (m, 2H), 7.46 (s, 2H), 7.44 – 7.39 (m, 2H), 7.38 – 7.34 (m, 2H), 7.12 (s, 1H), 3.74 (s, 3H), 2.35 (s, 6H), 1.54 (s, 9H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 159.6, 153.2, 150.9, 137.6, 137.4, 133.4,

128.7, 128.5, 127.9, 127.6, 127.3, 93.3, 84.0, 82.9, 53.2, 28.1, 27.6, 25.3, 21.1; HRMS (ESI-TOF): Calcd for $C_{28}H_{35}N_3O_6Na^+[M+Na]^+$ 532.2424, Found 532.2426.

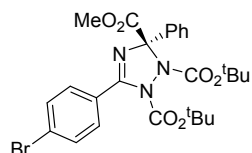


Entry	Retention Time	Area	% Area
1	8.895	9358900	49.63
2	9.608	9496835	50.37

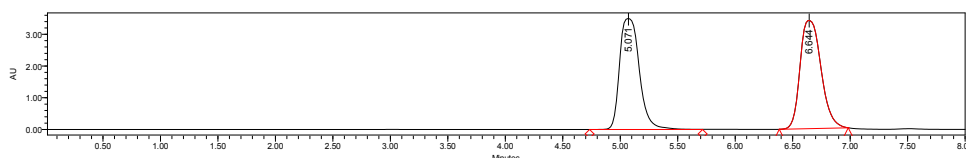


Entry	Retention Time	Area	% Area
1	8.800	143620	0.77
2	9.382	18605806	99.23

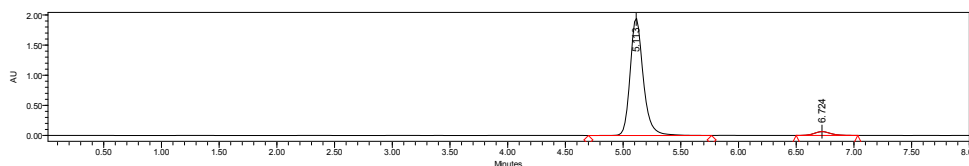
1,2-di-tert-butyl 3-methyl (R)-5-(4-bromophenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3fb**)



Colorless oil; 95% yield, 92% ee; $[\alpha]^{14.2}_D = +49.5$ (c 0.89, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 5.11 min, t (minor) = 6.72 min; 1H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.70 – 7.67 (m, 2H), 7.58 – 7.54 (m, 2H), 7.44 – 7.35 (m, 3H), 3.75 (s, 3H), 1.54 (s, 9H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 158.4, 153.2, 151.0, 137.3, 131.5, 131.1, 128.6, 127.9, 127.8, 127.2, 126.5, 93.5, 84.5, 83.0, 53.3, 28.1, 27.7; HRMS (ESI-TOF): Calcd for $C_{26}H_{30}^{78.9183}BrN_3O_6Na^+[M+Na]^+$ 582.1216, Found 582.1222; Calcd for $C_{26}H_{30}^{80.9163}BrN_3O_6Na^+[M+Na]^+$ 584.1195, Found 584.1208.

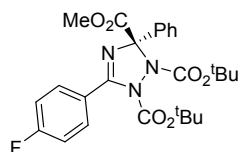


Entry	Retention Time	Area	% Area
1	5.071	41755135	49.20
2	6.644	43113273	50.80

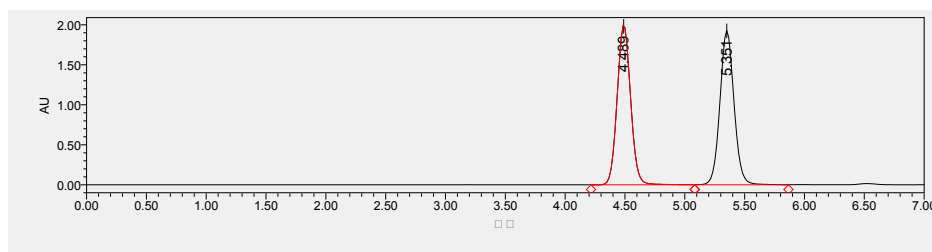


Entry	Retention Time	Area	% Area
1	5.113	15340963	96.08
2	6.724	625833	3.92

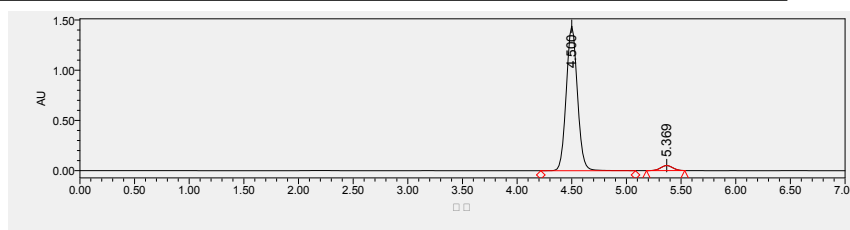
1,2-di-tert-butyl 3-methyl (R)-5-(4-fluorophenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3gb**)



Colorless oil; 94% yield, 92% ee; $[\alpha]^{14.2}_D = +31.9$ (c 0.94, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 4.50 min, t (minor) = 5.37 min; ^1H NMR (400 MHz, CDCl_3) δ 7.90 – 7.87 (m, 2H), 7.70 – 7.68 (m, 2H), 7.44 – 7.35 (m, 3H), 7.13 – 7.08 (m, 2H), 3.75 (s, 3H), 1.54 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.2, 164.8 (d, $J = 251.2$ Hz), 163.6, 158.2, 153.2, 151.0, 137.5, 132.4 (d, $J = 8.9$ Hz), 132.3, 128.6, 127.9, 127.2, 125.0 (d, $J = 3.2$ Hz), 115.1 (d, $J = 22.0$ Hz), 114.9, 93.3, 84.4, 83.0, 53.3, 28.1, 27.6; HRMS (ESI-TOF): Calcd for $\text{C}_{26}\text{H}_{30}\text{FN}_3\text{O}_6\text{Na}^+[\text{M}+\text{Na}]^+$ 522.2016, Found 522.2013.

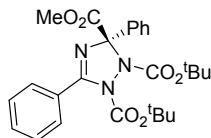


Entry	Retention Time	Area	% Area
1	4.489	15608607	49.75
2	5.351	15766048	50.25

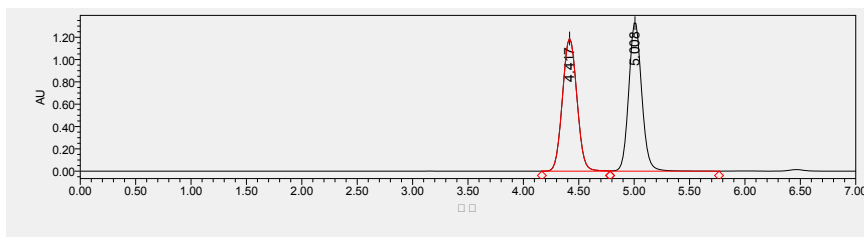


Entry	Retention Time	Area	% Area
1	4.500	10199405	96.36
2	5.369	384747	3.64

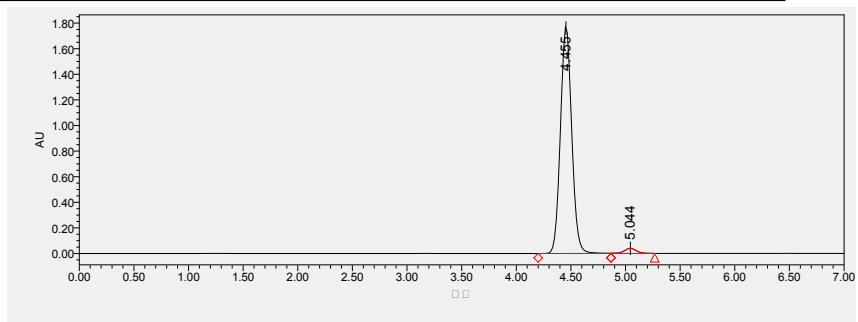
1,2-di-tert-butyl 3-methyl (R)-3,5-diphenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3hb**)



Colorless oil; 99% yield, 95% ee; $[\alpha]^{14.2}_D = +35.5$ (c 0.95, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 4.46 min, t (minor) = 5.04 min; ^1H NMR (400 MHz, CDCl_3) δ 7.87 – 7.85 (m, 2H), 7.73 – 7.70 (m, 2H), 7.52 – 7.47 (m, 1H), 7.44 – 7.41 (m, 4H), 7.40 – 7.34 (m, 1H), 3.75 (s, 3H), 1.55 (s, 9H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 159.2, 153.3, 150.9, 137.6, 131.6, 130.0, 129.0, 128.5, 127.9, 127.8, 127.3, 93.4, 84.2, 82.9, 53.2, 28.1, 27.6; HRMS (ESI-TOF): Calcd for $\text{C}_{26}\text{H}_{31}\text{N}_3\text{O}_6\text{Na}^+[\text{M}+\text{Na}]^+$ 504.2111, Found 504.2122.

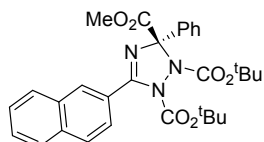


Entry	Retention Time	Area	% Area
1	4.417	10803594	49.92
2	5.008	10839419	50.08



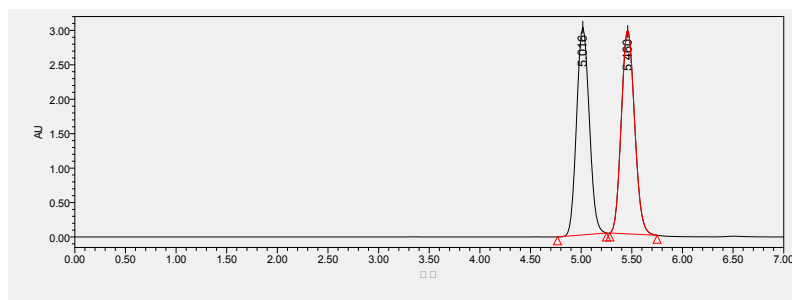
Entry	Retention Time	Area	% Area
1	4.455	12719216	97.65
2	5.044	305669	2.35

1,2-di-tert-butyl 3-methyl (R)-5-(naphthalen-2-yl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3ib**)

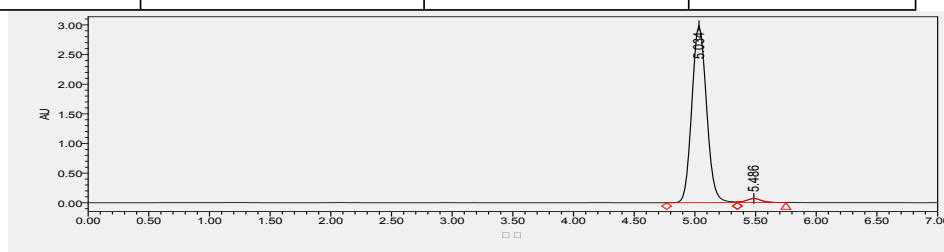


Colorless oil; 94% yield, 95% ee; $[\alpha]^{14.1}_D = +55.0$ (c 0.99, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 5.03 min, t (minor) = 5.49 min; ^1H NMR (400 MHz, CDCl_3) δ 8.41 (s, 1H), 7.94 – 7.91 (m, 2H), 7.88 – 7.84 (m, 2H), 7.78 – 7.76 (m, 2H), 7.57 – 7.49 (m, 2H), 7.47 – 7.43 (m, 2H), 7.41 – 7.37 (m, 1H), 3.76 (s, 3H), 1.57 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 159.3, 153.3, 151.0, 137.6, 134.8, 132.3, 130.8, 128.9, 128.6, 128.0, 127.8, 127.4, 127.3, 126.6,

126.3, 126.2, 93.4, 84.3, 83.0, 53.3, 28.1, 27.6; HRMS (ESI-TOF): Calcd for $C_{30}H_{33}N_3O_6Na^+[M+Na]^+$ 554.2267, Found 554.2263.

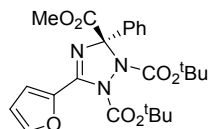


Entry	Retention Time	Area	% Area
1	5.016	26196083	49.31
2	5.460	26932346	50.69

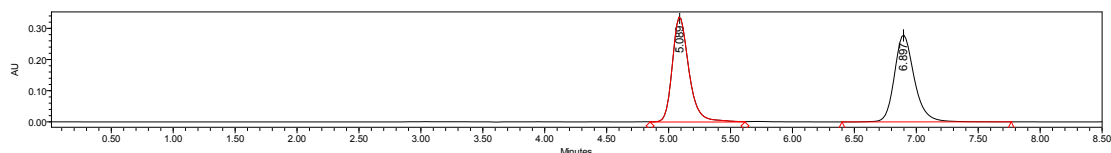


Entry	Retention Time	Area	% Area
1	5.034	25183538	97.66
2	5.486	603807	2.34

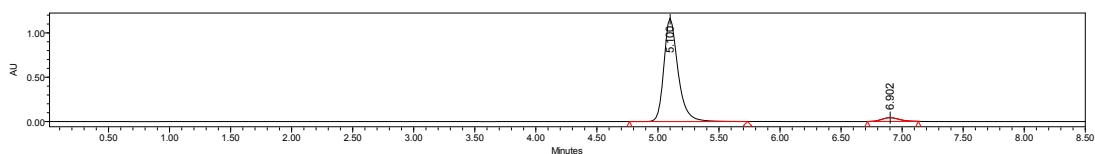
1,2-di-tert-butyl 3-methyl (R)-5-(furan-2-yl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3jb**)



Colorless oil; 83% yield, 91% ee; $[\alpha]^{14.1}_D = +67.3$ (c 0.78, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), *t* (major) = 5.10 min, *t* (minor) = 6.90 min; 1H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 2H), 7.60 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.26 – 7.24 (m, 1H), 6.54 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.74 (s, 3H), 1.52 (s, 9H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 153.0, 150.9, 149.4, 145.9, 142.7, 137.2, 128.6, 127.9, 127.3, 119.6, 111.8, 93.0, 84.4, 83.0, 53.2, 28.1, 27.7; HRMS (ESI-TOF): Calcd for $C_{24}H_{29}N_3O_7Na^+[M+Na]^+$ 494.1903, Found 494.1907.

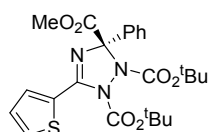


Entry	Retention Time	Area	% Area
1	5.089	3144709	50.28
2	6.897	3109494	49.72

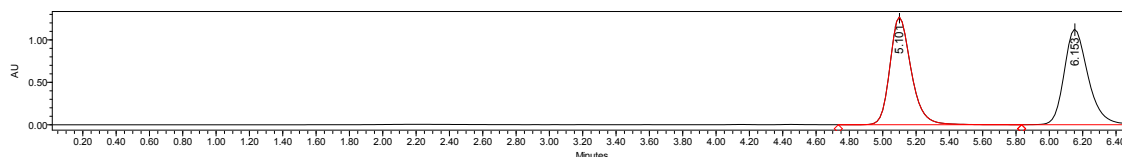


Entry	Retention Time	Area	% Area
1	5.100	9376375	95.65
2	6.902	426692	4.35

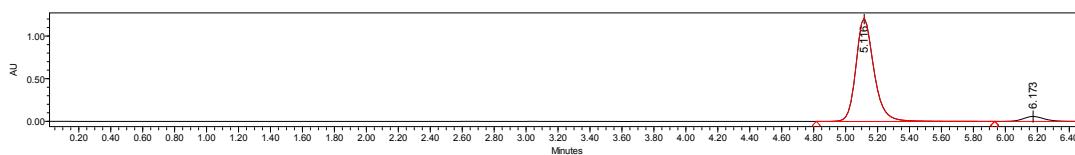
1,2-di-tert-butyl 3-methyl (R)-3-phenyl-5-(thiophen-2-yl)-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3kb**)



Colorless oil; 75% yield, 89% ee; $[\alpha]^{14.2}_D = +42.3$ (c 0.73, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 5.12 min, t (minor) = 6.17 min; ^1H NMR (400 MHz, CDCl_3) δ 7.80 (dd, $J = 4.0, 1.2$ Hz, 1H), 7.68 – 7.64 (m, 2H), 7.52 (dd, $J = 5.2, 1.2$ Hz, 1H), 7.41 – 7.32 (m, 3H), 7.11 (dd, $J = 4.8, 3.6$ Hz, 1H), 3.75 (s, 3H), 1.53 (s, 9H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.1, 153.4, 153.0, 151.1, 137.5, 134.5, 131.0, 130.3, 128.5, 127.8, 127.3, 127.2, 92.7, 84.4, 82.9, 53.2, 28.1, 27.7; HRMS (ESI-TOF): Calcd for $\text{C}_{24}\text{H}_{29}\text{N}_3\text{O}_6\text{SNa}^+[\text{M}+\text{Na}]^+$ 510.1675, Found 510.1666.

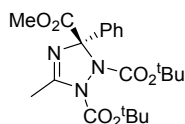


Entry	Retention Time	Area	% Area
1	5.101	11203643	50.06
2	6.153	11175280	49.94

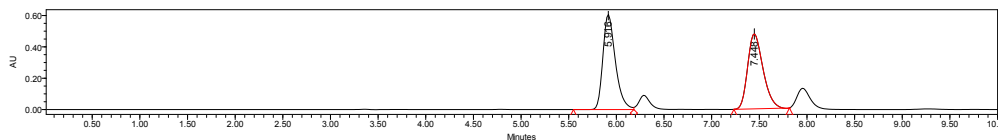


Entry	Retention Time	Area	% Area
1	5.116	9450368	94.56
2	6.173	544078	5.44

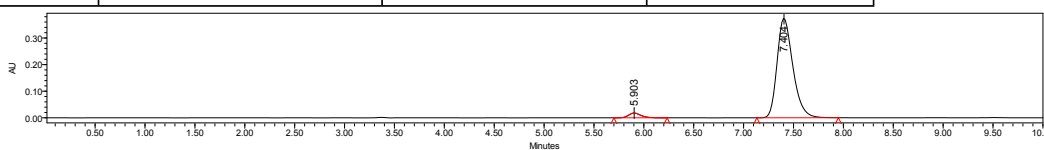
1,2-di-tert-butyl 3-methyl (R)-5-methyl-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3lb**)



White solid; 90% yield, 92% ee; $[\alpha]^{14.3}_D = -48.4$ (c 0.75, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 20/80, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 7.40 min, t (minor) = 5.90 min; ^1H NMR (400 MHz, CDCl_3) δ 7.63 – 7.61 (m, 2H), 7.40 – 7.31 (m, 3H), 3.75 (s, 3H), 2.40 (s, 3H), 1.51 (s, 9H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 156.5, 153.6, 149.7, 137.8, 128.4, 127.8, 127.2, 93.5, 84.2, 83.1, 53.2, 28.0, 27.9, 17.2; HRMS (ESI-TOF): Calcd for $\text{C}_{21}\text{H}_{29}\text{N}_3\text{O}_6\text{Na}^+[\text{M}+\text{Na}]^+$ 442.1954, Found 442.1945.

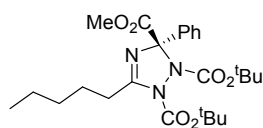


Entry	Retention Time	Area	% Area
1	5.916	5507141	50.66
2	7.448	5362739	49.34

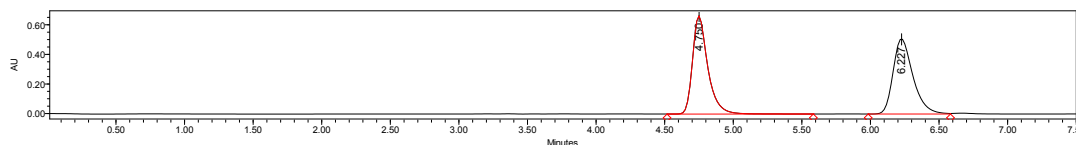


Entry	Retention Time	Area	% Area
1	5.903	153747	3.61
2	7.404	4110082	96.39

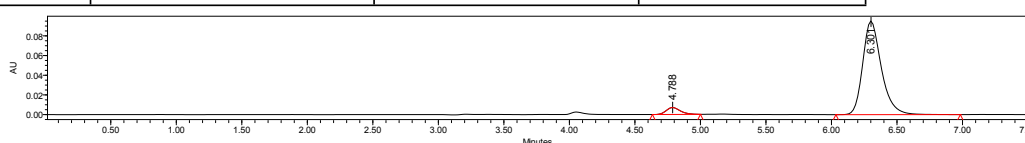
1,2-di-tert-butyl 3-methyl (R)-5-pentyl-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3mb**)



Colorless oil; 81% yield, 89% ee; $[\alpha]^{14.1}_D = -24.7$ (c 0.76, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 20/80, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 6.30 min, t (minor) = 4.79 min; ^1H NMR (400 MHz, CDCl_3) δ 7.64 – 7.61 (m, 2H), 7.40 – 7.30 (m, 3H), 3.74 (s, 3H), 2.85 – 2.61 (m, 2H), 1.79 – 1.71 (m, 2H), 1.50 (s, 9H), 1.48 (s, 9H), 1.40 – 1.32 (m, 4H), 0.90 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.6, 160.0, 153.7, 149.8, 138.0, 128.3, 127.8, 127.2, 93.4, 84.0, 82.9, 53.1, 31.1, 30.3, 28.0, 27.9, 26.0, 22.3, 14.0; HRMS (ESI-TOF): Calcd for $\text{C}_{21}\text{H}_{29}\text{N}_3\text{O}_6\text{Na}^+[\text{M}+\text{Na}]^+$ 498.2580, Found 498.2585.



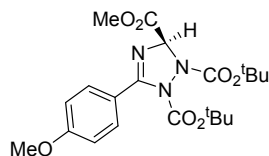
Entry	Retention Time	Area	% Area
1	4.750	5116683	50.03
2	6.227	5111116	49.97



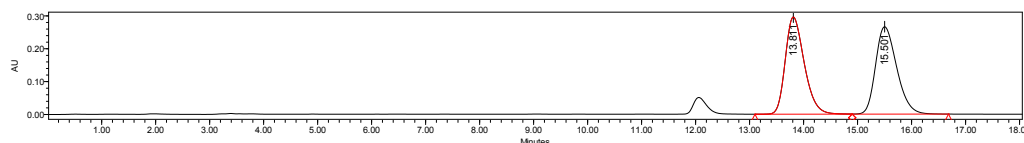
Entry	Retention Time	Area	% Area
1	4.790		
2	6.300		

1	4.788	52435	5.30
2	6.301	936937	94.70

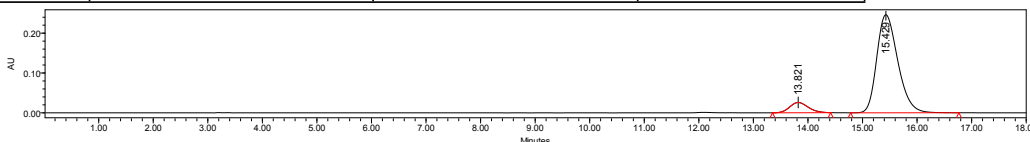
1,2-di-tert-butyl 3-methyl (R)-5-(4-methoxyphenyl)-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3nb**)



Colorless oil; 91% yield, 83% ee; $[\alpha]^{14.1}_D = +85.6$ (c 0.44, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 20/80, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 15.43 min, t (minor) = 13.82 min; ^1H NMR (400 MHz, CDCl_3) δ 7.81 – 7.71 (m, 2H), 6.94 – 6.90 (m, 2H), 6.12 (s, 1H), 3.84 (s, 3H), 3.77 (s, 3H), 1.52 (s, 9H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.3, 162.5, 160.9, 155.3, 151.7, 131.7, 121.5, 113.3, 83.5, 83.1, 81.6, 55.4, 52.7, 28.1, 27.7; HRMS (ESI-TOF): Calcd for $\text{C}_{21}\text{H}_{29}\text{N}_3\text{O}_7\text{Na}^+[\text{M}+\text{Na}]^+$ 458.1903, Found 458.1906.

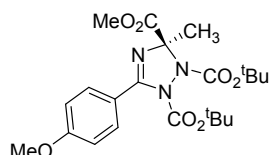


Entry	Retention Time	Area	% Area
1	13.811	7214892	49.97
2	15.501	7224775	50.03

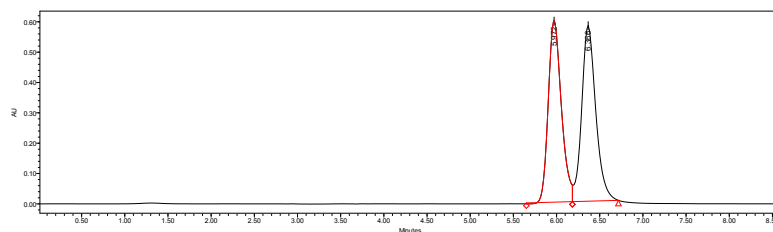


Entry	Retention Time	Area	% Area
1	13.821	605936	8.44
2	15.429	6577324	91.56

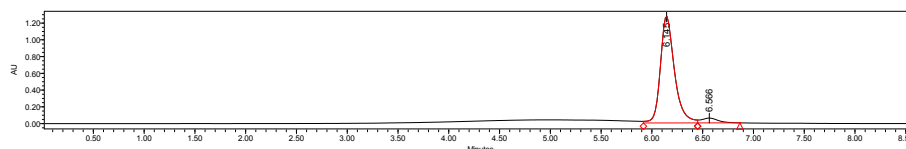
1,2-di-tert-butyl 3-methyl (R)-5-(4-methoxyphenyl)-3-methyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3ob**)



White solid; 84% yield, 89% ee; $[\alpha]^{14.2}_D = +83.0$ (c 0.75, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 5/95, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 6.14 min, t (minor) = 6.57 min; ^1H NMR (400 MHz, CDCl_3) δ 7.80 – 7.76 (m, 2H), 6.92 – 6.88 (m, 2H), 3.84 (s, 3H), 3.72 (s, 3H), 1.74 (s, 3H), 1.49 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.9, 162.3, 158.8, 152.3, 151.7, 131.7, 121.4, 113.1, 89.0, 84.1, 82.2, 55.4, 52.8, 28.1, 27.7, 23.0; HRMS (ESI-TOF): Calcd for $\text{C}_{22}\text{H}_{31}\text{N}_3\text{O}_7\text{Na}^+[\text{M}+\text{Na}]^+$ 472.2060, Found 472.2069.

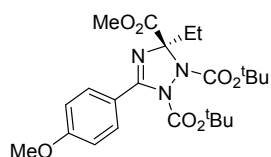


Entry	Retention Time	Area	% Area
1	5.972	6312743	49.04
2	6.366	6560431	50.96

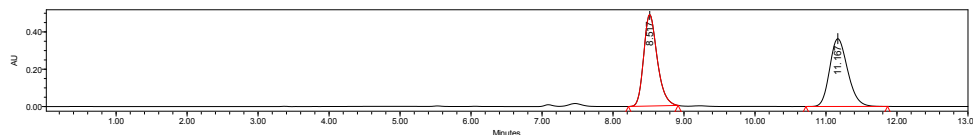


Entry	Retention Time	Area	% Area
1	6.145	12242732	94.88
2	6.566	660476	5.12

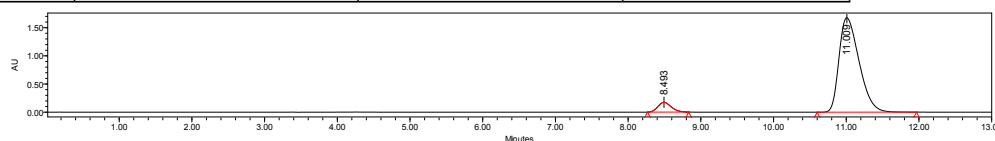
1,2-di-tert-butyl 3-methyl (R)-3-ethyl-5-(4-methoxyphenyl)-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3pb**)



Colorless oil; 95% yield, 87% ee; $[\alpha]^{14.1}_D = +79.5$ (c 0.87, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 20/80, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 11.01 min, t (minor) = 8.49 min; ^1H NMR (400 MHz, CDCl_3) δ 7.81 – 7.76 (m, 2H), 6.92 – 6.88 (m, 2H), 3.83 (s, 3H), 3.70 (s, 3H), 2.19 (q, $J = 7.6$ Hz, 2H), 1.48 (s, 9H), 1.33 (s, 9H), 0.89 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.9, 162.2, 159.0, 151.3, 131.5, 121.6, 113.1, 92.4, 84.0, 82.2, 55.4, 52.7, 28.1, 27.7, 6.7; HRMS (ESI-TOF): Calcd for $\text{C}_{23}\text{H}_{33}\text{N}_3\text{O}_7\text{Na}^+[\text{M}+\text{Na}]^+$ 486.2216, Found 486.2224.



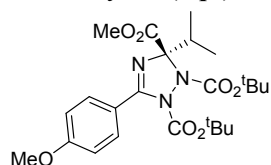
Entry	Retention Time	Area	% Area
1	8.517	6483560	50.37
2	11.167	6388289	49.63



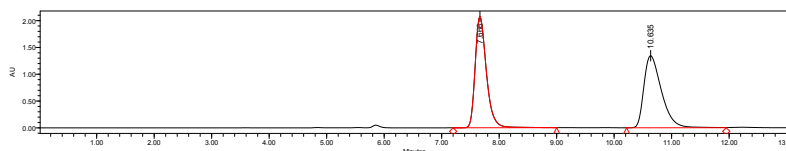
Entry	Retention Time	Area	% Area
1	8.493	2204631	6.43

2	11.009	32064456	93.57
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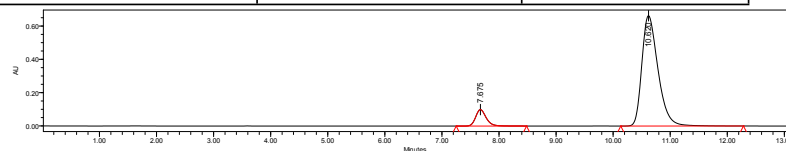
1,2-di-tert-butyl 3-methyl (R)-3-isopropyl-5-(4-methoxyphenyl)-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3qb**)



Colorless oil; 89% yield, 82% ee; $[\alpha]^{14.1}_D = +79.0$ (c 0.30, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 20/80, 1.0 mL/min, $\lambda = 254$ nm), *t* (major) = 10.62 min, *t* (minor) = 7.68 min; ^1H NMR (400 MHz, CDCl_3) δ 7.79 – 7.75 (m, 2H), 6.93 – 6.89 (m, 2H), 3.83 (s, 3H), 3.68 (s, 3H), 2.64 – 2.56 (m, 1H), 1.49 (s, 9H), 1.34 (s, 9H), 1.11 (d, $J = 6.8$ Hz, 3H), 0.94 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.0, 162.2, 158.3, 151.2, 131.5, 121.6, 113.2, 94.9, 83.7, 82.3, 55.4, 52.5, 33.6, 28.0, 27.7, 17.3, 16.3; HRMS (ESI-TOF): Calcd for $\text{C}_{24}\text{H}_{35}\text{N}_3\text{O}_7\text{Na}^+[\text{M}+\text{Na}]^+$ 500.2373, Found 500.2379.

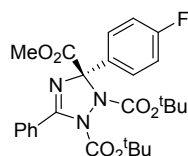


Entry	Retention Time	Area	% Area
1	7.666	28091251	49.66
2	10.635	28477020	50.34



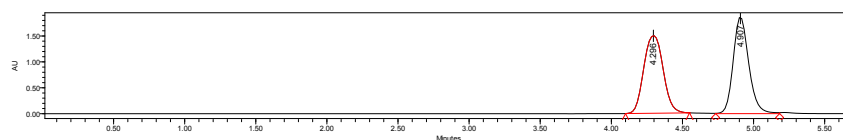
Entry	Retention Time	Area	% Area
1	7.675	1260761	8.85
2	10.620	12979841	91.15

1,2-di-tert-butyl 3-methyl (R)-3-(4-fluorophenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3rb**)

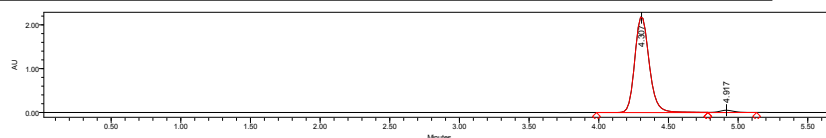


Colorless oil; 94% yield, 95% ee; $[\alpha]^{14.1}_D = +42.4$ (c 0.93, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), *t* (major) = 4.31 min, *t* (minor) = 4.92 min; ^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.83 (m, 2H), 7.71 – 7.67 (m, 2H), 7.52 – 7.48 (m, 1H), 7.44 – 7.40 (m, 2H), 7.11 – 7.07 (m, 2H), 3.74 (s, 3H), 1.54 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.2, 162.8 (d, $J = 245.7$ Hz), 159.3, 153.3, 150.9, 133.6 (d, $J = 3.1$ Hz), 133.5, 131.7, 129.9, 129.2 (d, $J = 8.2$ Hz), 128.9, 127.9, 114.8 (d, $J = 21.5$ Hz), 92.8, 84.3, 83.1, 53.3, 28.1, 27.6; HRMS (ESI-TOF): Calcd for

C₂₆H₃₀FN₃O₆Na⁺[M+Na]⁺ 522.2016, Found 522.2009.

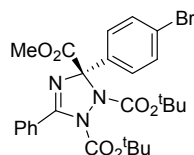


Entry	Retention Time	Area	% Area
1	4.296	14157624	49.89
2	4.907	14217357	50.11

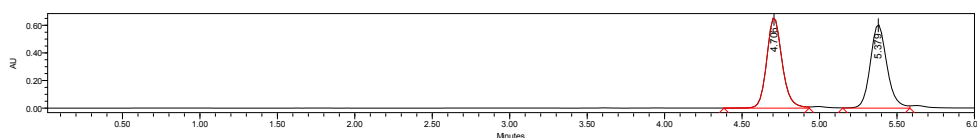


Entry	Retention Time	Area	% Area
1	4.307	15790803	97.63
2	4.917	383158	2.37

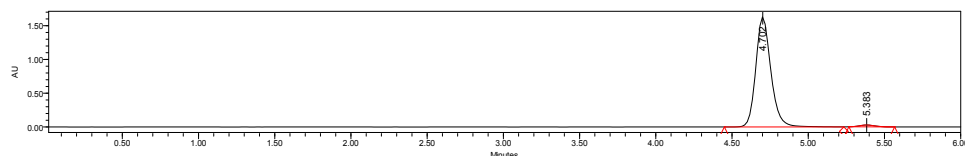
1,2-di-tert-butyl 3-methyl (R)-3-(4-bromophenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3sb**)



Colorless oil; 81% yield, 96% ee; $[\alpha]^{14.1}_D = +19.7$ (c 0.90, CH₂Cl₂); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), *t* (major) = 4.70 min, *t* (minor) = 5.38 min; ¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.82 (m, 2H), 7.60 – 7.48 (m, 5H), 7.42 (t, *J* = 7.2 Hz, 2H), 3.74 (s, 3H), 1.54 (s, 9H), 1.26 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 167.9, 159.4, 153.2, 150.7, 136.8, 131.8, 131.1, 129.9, 129.1, 128.8, 127.9, 122.8, 92.9, 84.4, 83.1, 53.4, 28.1, 27.6; HRMS (ESI-TOF): Calcd for C₂₆H₃₀^{78,9183}BrN₃O₆Na⁺ [M+Na]⁺ 582.1216, Found 582.1215; Calcd for C₂₆H₃₀^{80,9163}BrN₃O₆Na⁺ [M+Na]⁺ 584.1195, Found 584.1207.



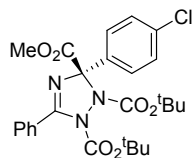
Entry	Retention Time	Area	% Area
1	4.706	4530996	50.10
2	5.379	4512859	49.90



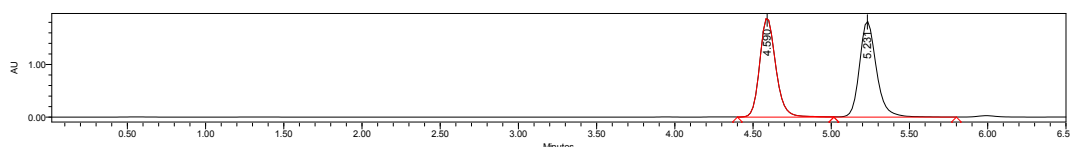
Entry	Retention Time	Area	% Area
1	4.702	11243457	98.36

2	5.383	187942	1.64
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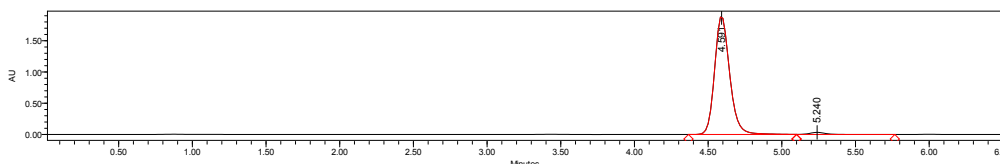
1,2-di-tert-butyl 3-methyl (R)-3-(4-chlorophenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3tb**)



Colorless oil; 88% yield, 96% ee; $[\alpha]^{14.1}_D = +25.5$ (c 0.90, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), *t* (major) = 4.59 min, *t* (minor) = 5.24 min; ^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.82 (m, 2H), 7.67 – 7.63 (m, 2H), 7.52 – 7.48 (m, 1H), 7.44 – 7.42 (m, 2H), 7.40 – 7.36 (m, 2H), 3.74 (s, 3H), 1.54 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.0, 159.4, 153.2, 150.7, 136.3, 134.5, 131.8, 129.9, 128.8, 128.1, 127.9, 92.9, 84.4, 83.1, 53.3, 28.1, 27.6; HRMS (ESI-TOF): Calcd for $\text{C}_{26}\text{H}_{31}^{34.9689}\text{ClN}_3\text{O}_6[\text{M}+\text{H}]^+$ 516.1901, Found 516.1900; Calcd for $\text{C}_{26}\text{H}_{31}^{36.9659}\text{ClN}_3\text{O}_6[\text{M}+\text{H}]^+$ 518.1872, Found 518.1869.

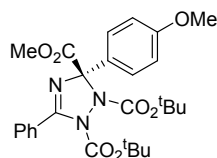


Entry	Retention Time	Area	% Area
1	4.590	13481202	49.62
2	5.231	13688222	50.38



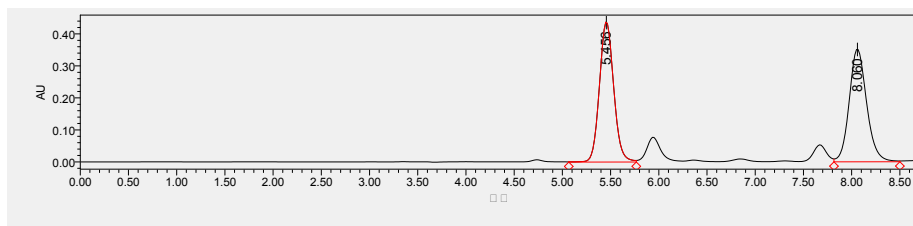
Entry	Retention Time	Area	% Area
1	4.591	13491193	98.08
2	5.240	264360	1.92

1,2-di-tert-butyl 3-methyl (R)-3-(4-methoxyphenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3ub**)

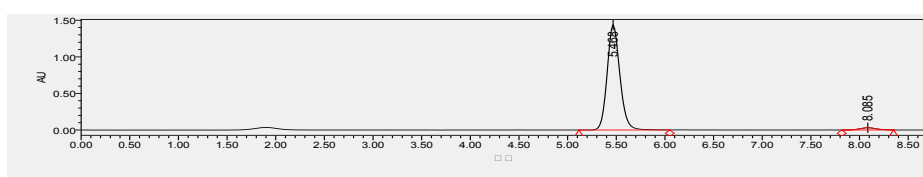


Colorless oil; 74% yield, 94% ee; $[\alpha]^{14.1}_D = +28.5$ (c 0.61, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), *t* (major) = 5.47 min, *t* (minor) = 8.08 min; ^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.83 (m, 2H), 7.64 – 7.60 (m, 2H), 7.50 – 7.46 (m, 1H), 7.43 – 7.39 (m, 2H), 6.97 – 6.91 (m, 2H), 3.83 (s, 3H), 3.74

(s, 3H), 1.54 (s, 9H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 159.7, 159.0, 153.3, 150.9, 131.6, 129.9, 129.7, 129.1, 128.5, 127.8, 113.3, 93.1, 84.1, 82.8, 55.2, 53.2, 28.1, 27.6; HRMS (ESI-TOF): Calcd for $\text{C}_{27}\text{H}_{33}\text{N}_3\text{O}_7\text{Na}^+[\text{M}+\text{Na}]^+$ 534.2216, Found 534.2203.

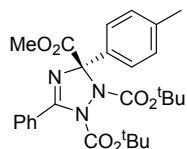


Entry	Retention Time	Area	% Area
1	5.456	4497471	50.36
2	8.060	4432372	49.64

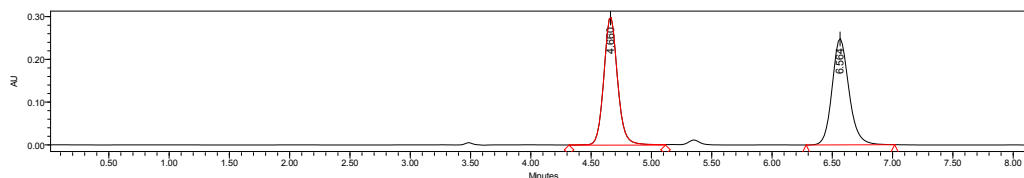


Entry	Retention Time	Area	% Area
1	5.468	13078724	97.36
2	8.085	354287	2.64

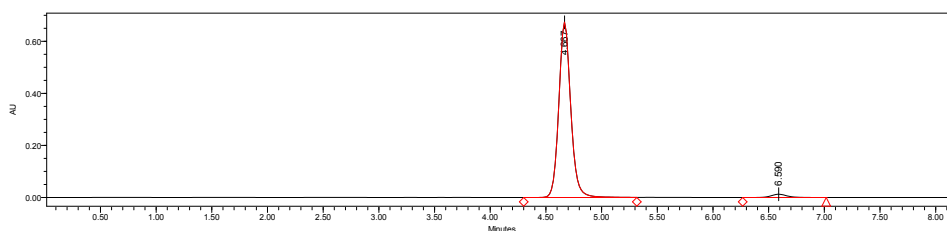
1,2-di-tert-butyl 3-methyl (R)-5-phenyl-3-(p-tolyl)-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3vb**)



Colorless oil; 99% yield, 95% ee; $[\alpha]^{14.1}_D = +27.4$ (c 0.93, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 4.67 min, t (minor) = 6.59 min; ^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.84 (m, 2H), 7.61 – 7.59 (m, 2H), 7.51 – 7.47 (m, 1H), 7.43 – 7.39 (m, 2H), 7.24 – 7.21 (m, 2H), 3.74 (s, 3H), 2.38 (s, 3H), 1.54 (s, 9H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.4, 159.0, 153.3, 150.9, 138.3, 134.6, 131.6, 129.9, 129.1, 128.6, 127.8, 127.2, 93.4, 84.1, 82.8, 53.2, 28.1, 27.6, 21.2; HRMS (ESI-TOF): Calcd for $\text{C}_{27}\text{H}_{33}\text{N}_3\text{O}_6\text{Na}^+[\text{M}+\text{Na}]^+$ 518.2267, Found 518.2260.

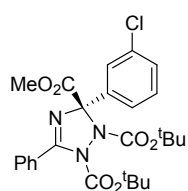


Entry	Retention Time	Area	% Area
1	4.660	2382395	49.73
2	6.564	2408126	50.27

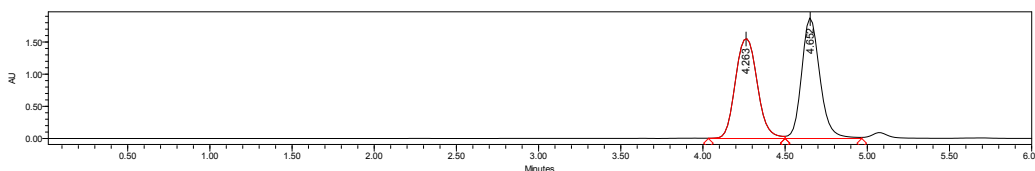


Entry	Retention Time	Area	% Area
1	4.667	5024142	97.60
2	6.590	123648	2.40

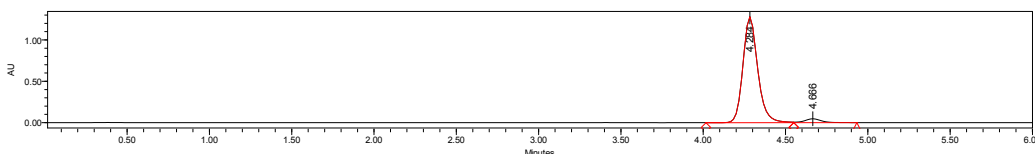
1,2-di-tert-butyl 3-methyl (R)-3-(3-chlorophenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(3H)-ntricarboxylate (**3wb**)



Colorless oil; 70% yield, 92% ee; $[\alpha]^{14.1}_D = +35.8$ (c 0.65, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 4.28 min, t (minor) = 4.67 min; ^1H NMR (400 MHz, CDCl_3) δ 7.87 – 7.85 (m, 2H), 7.71 – 7.70 (m, 1H), 7.63 – 7.58 (m, 1H), 7.53 – 7.49 (m, 1H), 7.45 – 7.41 (m, 2H), 7.36 – 7.33 (m, 2H), 3.75 (s, 3H), 1.55 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.9, 159.6, 153.1, 150.8, 139.7, 133.8, 131.9, 130.1, 129.3, 128.7, 128.7, 127.9, 127.4, 125.8, 92.7, 84.5, 83.2, 53.4, 28.1, 27.6; HRMS (ESI-TOF): Calcd for $\text{C}_{26}\text{H}_{30}^{34,9689}\text{ClN}_3\text{O}_6\text{Na}^+[\text{M}+\text{Na}]^+$ 538.1721, Found 538.1716; Calcd for $\text{C}_{26}\text{H}_{30}^{36,9659}\text{ClN}_3\text{O}_6\text{Na}^+[\text{M}+\text{Na}]^+$ 540.1691, Found 540.1699.

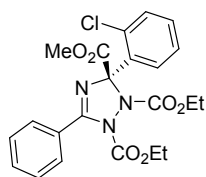


Entry	Retention Time	Area	% Area
1	4.263	14420104	49.91
2	4.652	14472713	50.09

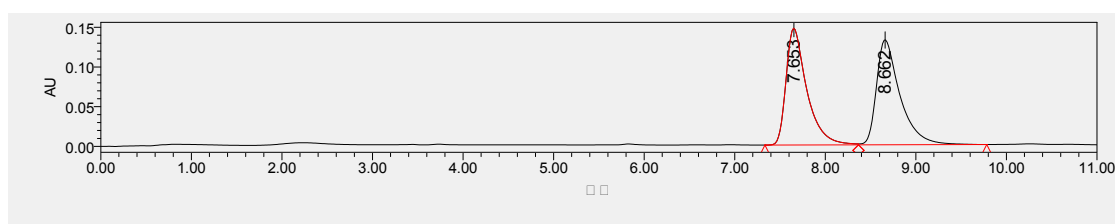


Entry	Retention Time	Area	% Area
1	4.284	7980657	96.09
2	4.666	324918	3.91

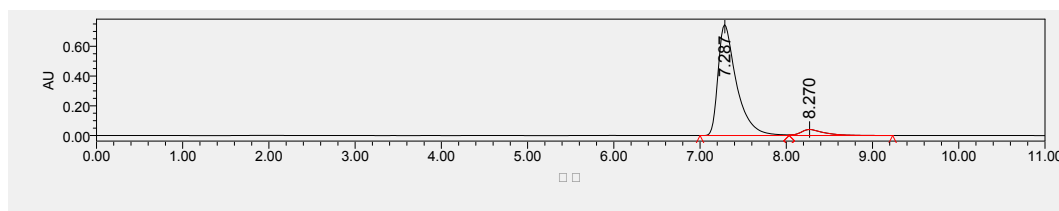
1,2-diethyl 3-methyl (R)-3-(2-chlorophenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3xa**)



Colorless oil; 75% yield, 87% ee; $[\alpha]^{18.7}_D = +65.2$ (c 0.60, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IB column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 7.29 min, t (minor) = 8.27 min; ^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.84 (m, 2H), 7.81 – 7.84 (m, 1H), 7.52 – 7.46 (m, 2H), 7.42 – 7.38 (m, 2H), 7.35 – 7.26 (m, 2H), 4.31 – 4.06 (m, 4H), 3.80 (s, 3H), 1.30 (t, $J = 7.0$ Hz, 3H), 1.12 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.6, 158.7, 154.7, 152.1, 134.2, 132.0, 131.3, 130.2, 130.2, 128.2, 127.8, 126.6, 94.5, 63.9, 63.4, 53.5, 14.3, 13.9; HRMS (ESI-TOF): Calcd for $\text{C}_{22}\text{H}_{22}^{34.9689}\text{ClN}_3\text{O}_6\text{Na}^+[\text{M}+\text{Na}]^+$ 482.1095, Found 482.1099; Calcd for $\text{C}_{22}\text{H}_{22}^{36.9659}\text{ClN}_3\text{O}_6\text{Na}^+[\text{M}+\text{Na}]^+$ 484.1065, Found 484.1080.

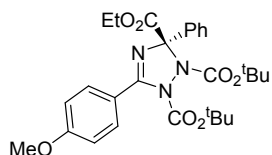


Entry	Retention Time	Area	% Area
1	7.653	2339238	49.52
2	8.662	2384131	50.48



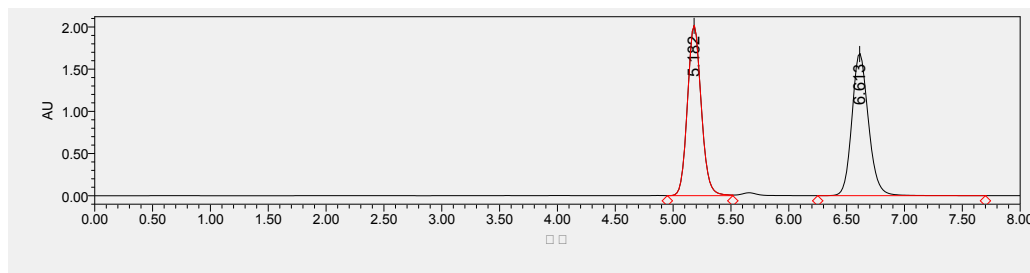
Entry	Retention Time	Area	% Area
1	7.287	11047728	93.52
2	8.270	764983	6.48

1,2-di-tert-butyl 3-ethyl (R)-5-(4-methoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3yb**)

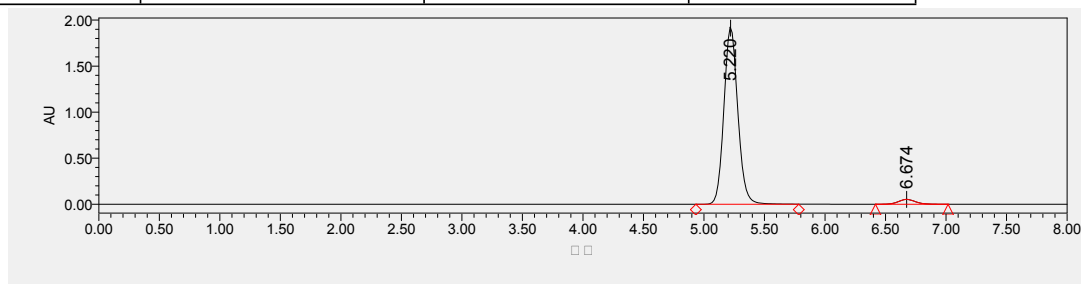


Colorless oil; 99% yield, 94% ee; $[\alpha]^{14.0}_D = +72.6$ (c 1.03, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IA column (*i*PrOH/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm), t (major) = 5.22 min, t (minor) = 6.67 min; ^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.82 (m, 2H), 7.71 – 7.69 (m, 2H), 7.42 – 7.32 (m, 3H), 6.94 – 6.91 (m, 2H), 4.24 – 4.15 (m, 2H), 3.84 (s, 3H), 1.54 (s, 9H), 1.30 (s, 9H), 1.22 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.9, 162.3, 158.6,

153.1, 151.3, 137.9, 131.9, 128.3, 127.8, 127.3, 121.2, 113.2, 93.0, 84.0, 82.6, 62.6, 55.4, 28.1, 27.7, 13.8; HRMS (ESI-TOF): Calcd for C₂₈H₃₅N₃O₇Na⁺[M+Na]⁺ 548.2373, Found 548.2367.



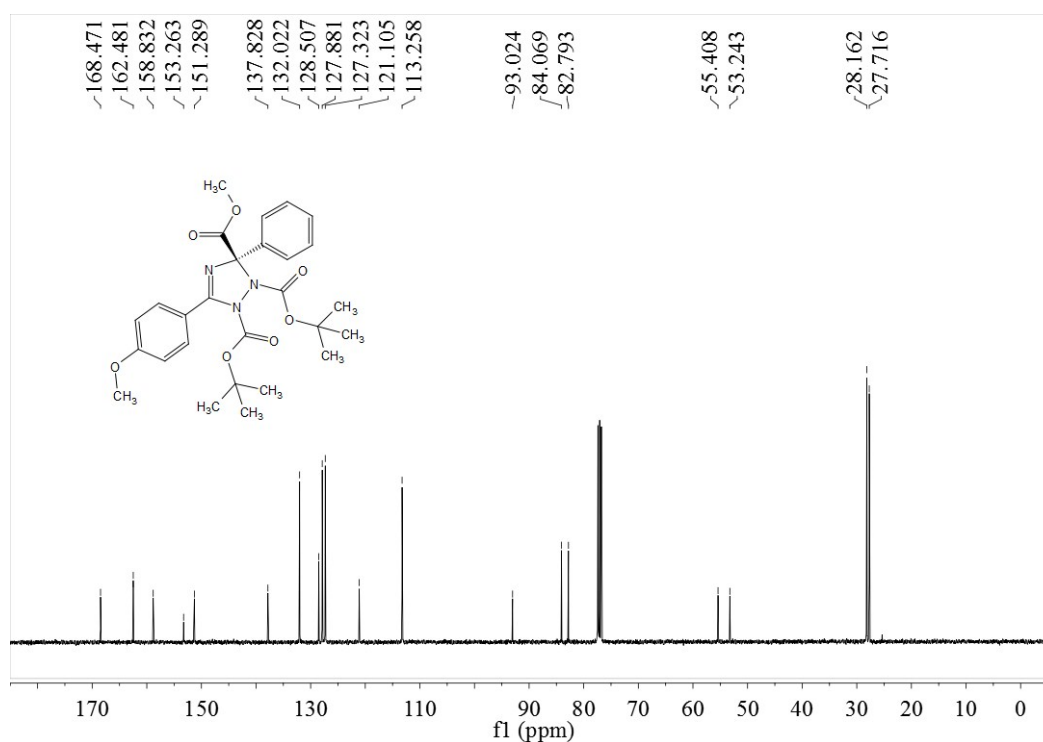
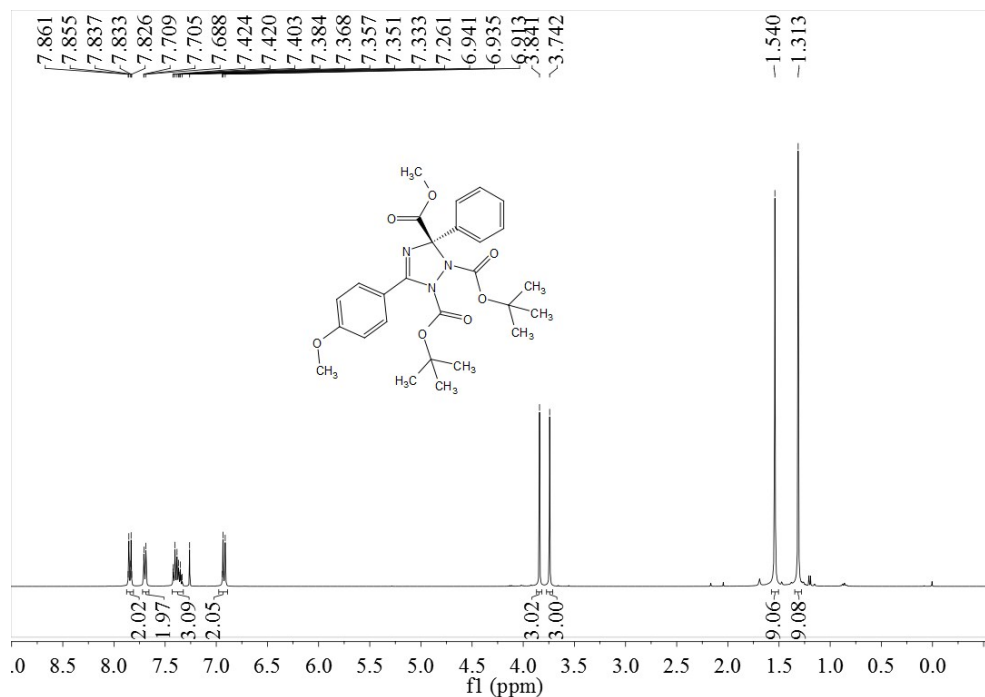
Entry	Retention Time	Area	% Area
1	5.182	16732563	49.84
2	6.613	16843098	50.16



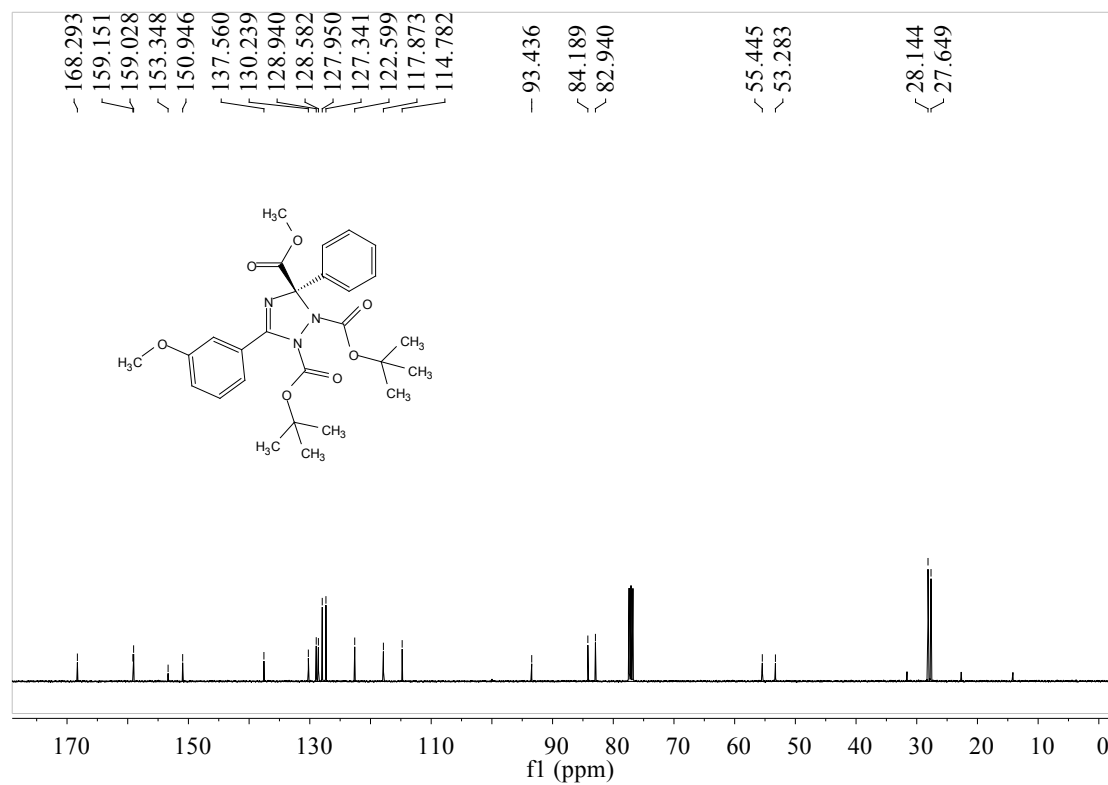
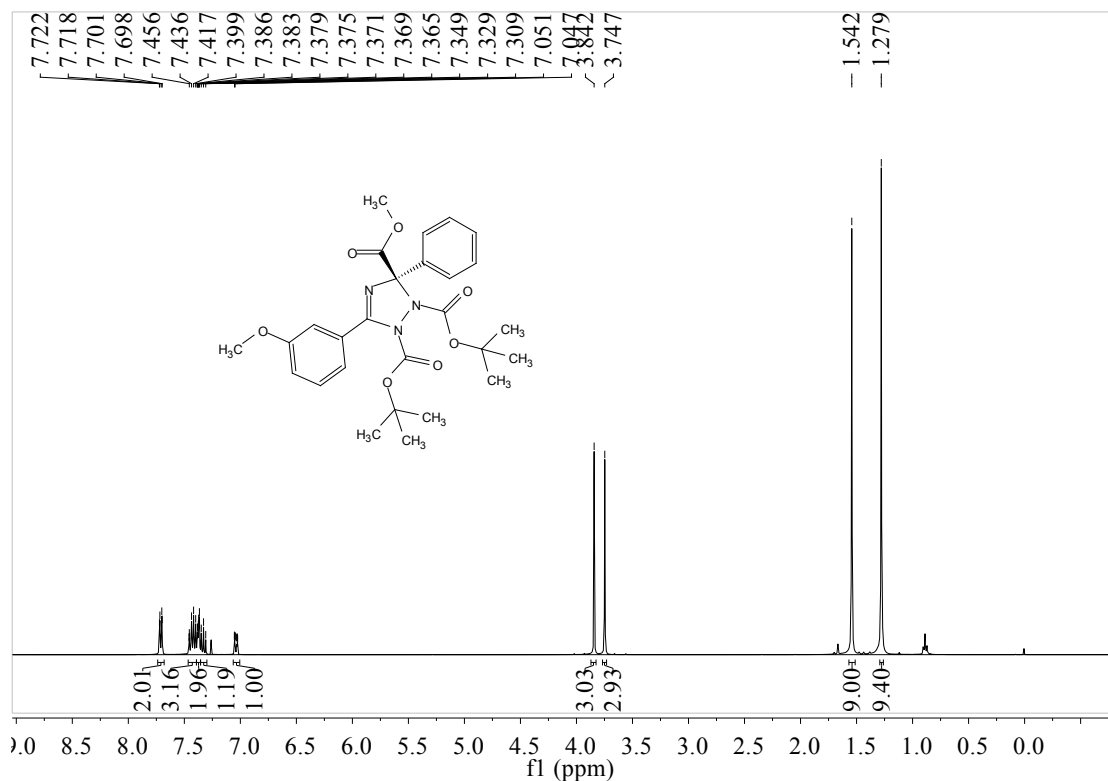
Entry	Retention Time	Area	% Area
1	5.220	15357023	96.75
2	6.674	515219	3.25

(H) Copies of NMR spectra for the products

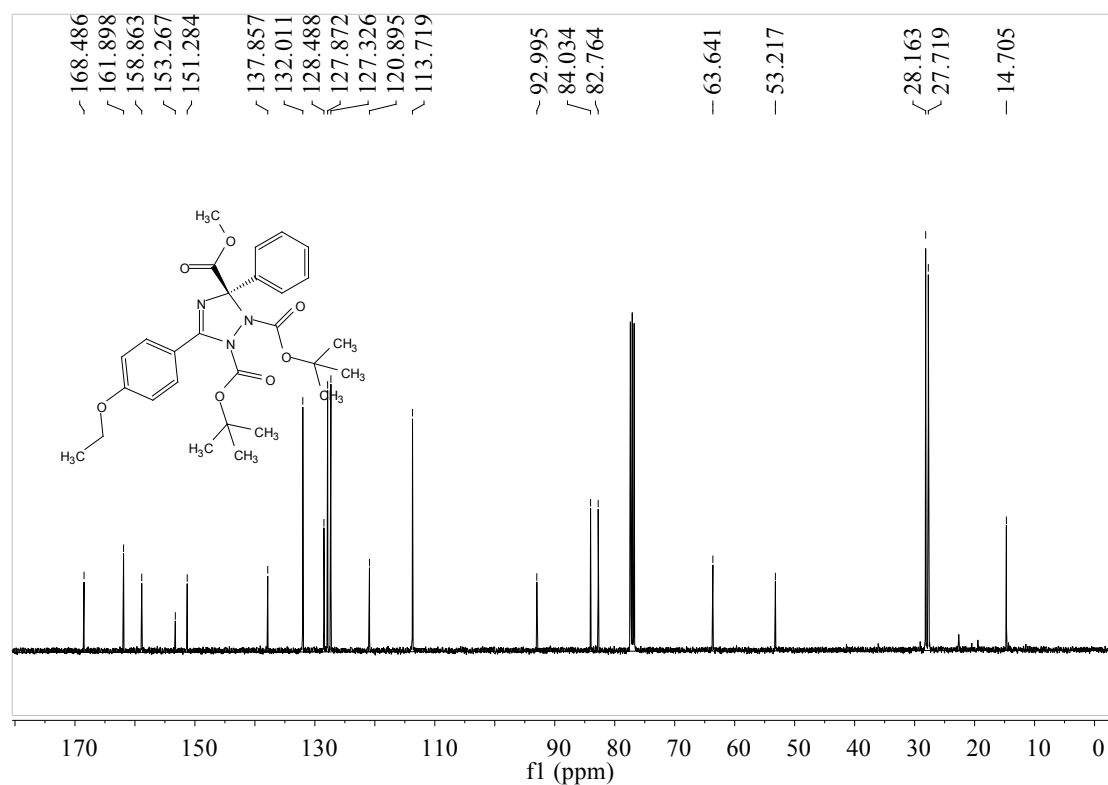
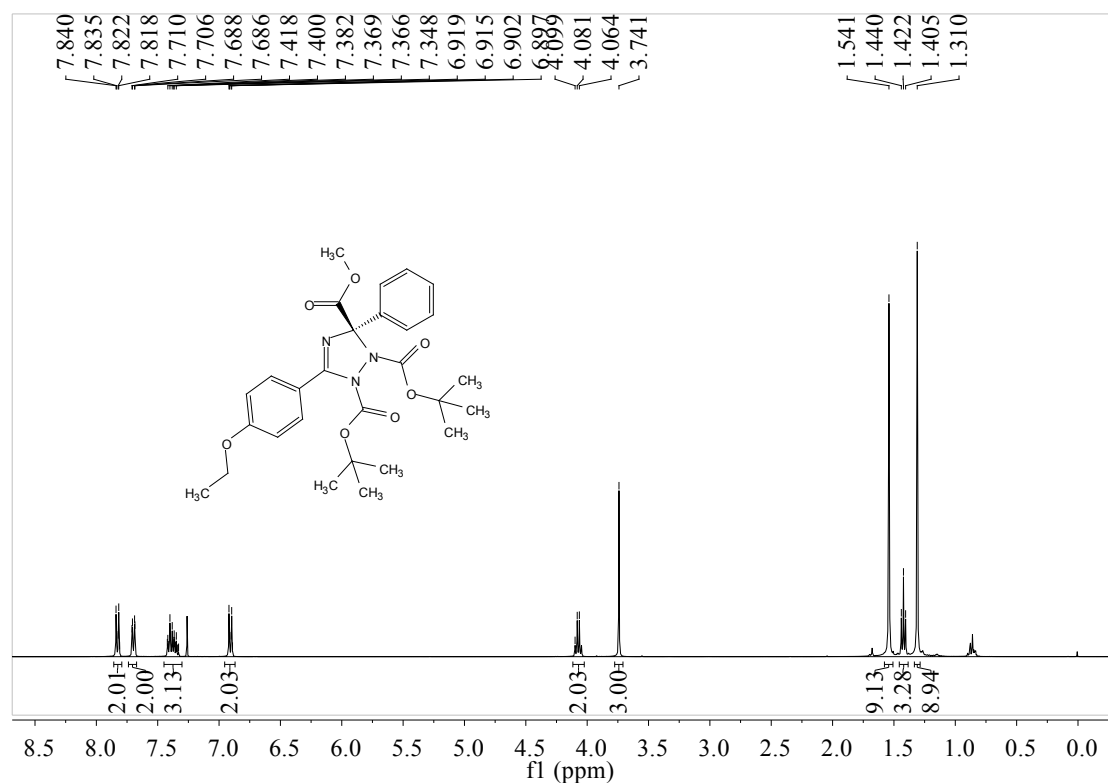
1,2-di-tert-butyl 3-methyl (R)-5-(4-methoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3ab**)



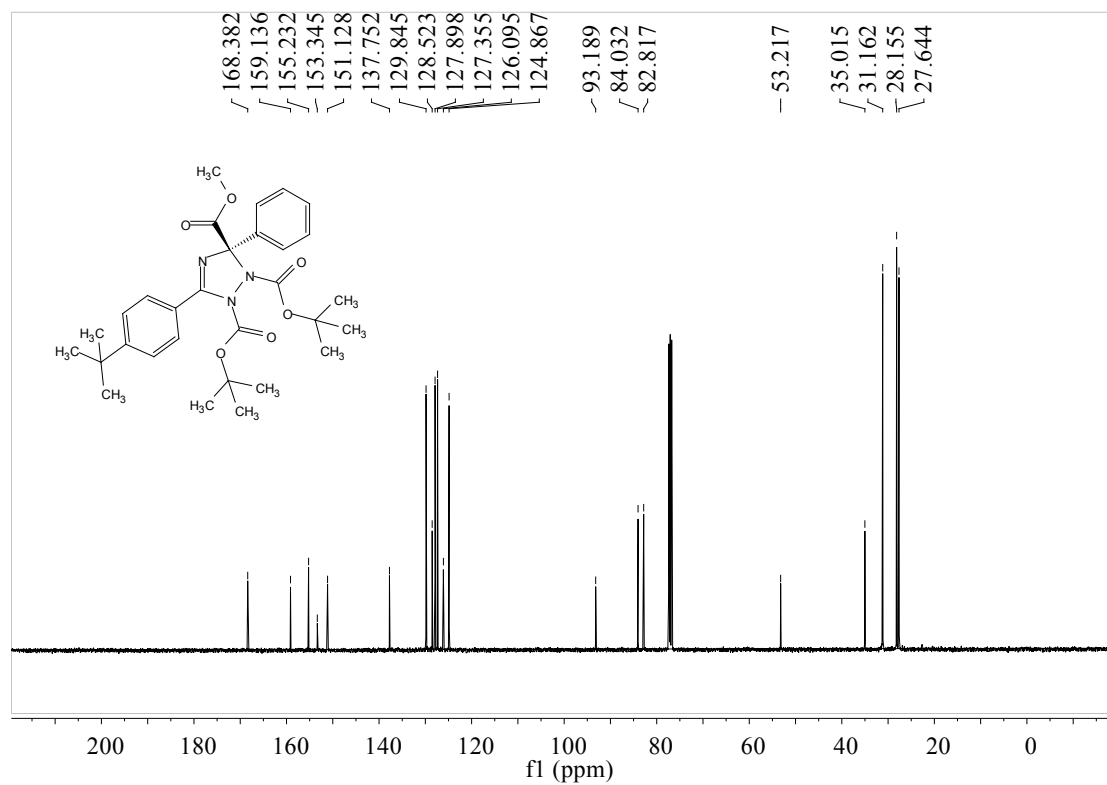
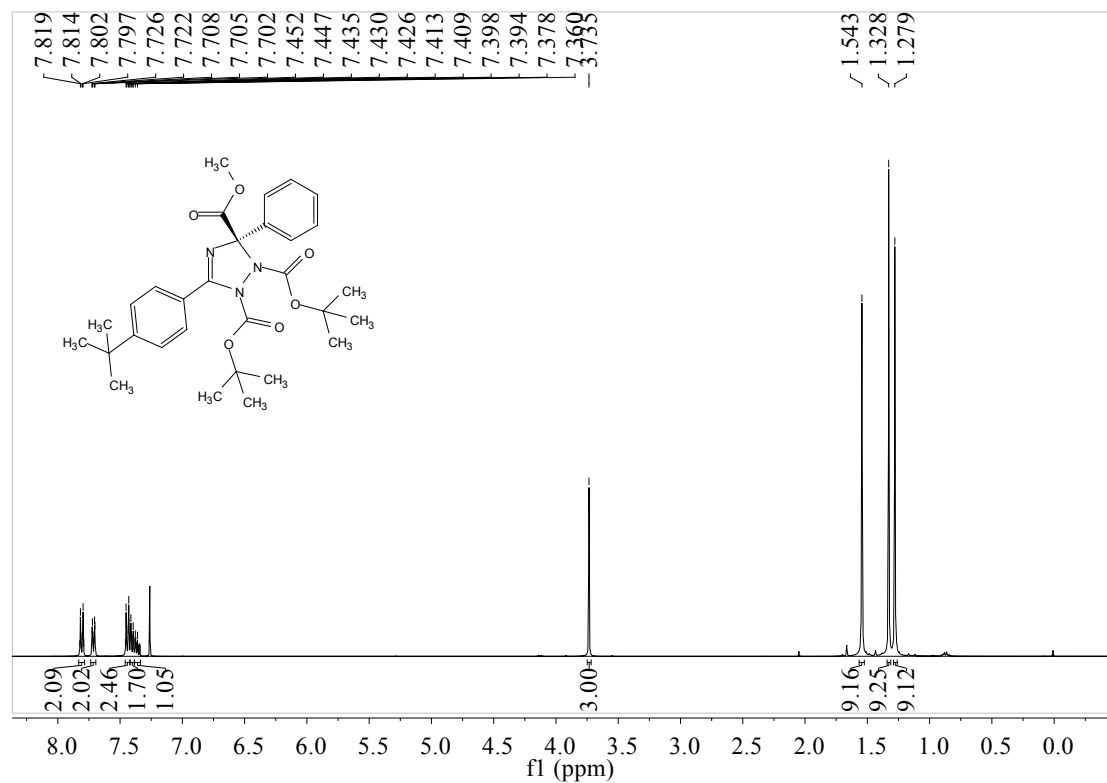
1,2-di-tert-butyl 3-methyl (R)-5-(3-methoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3bb**)



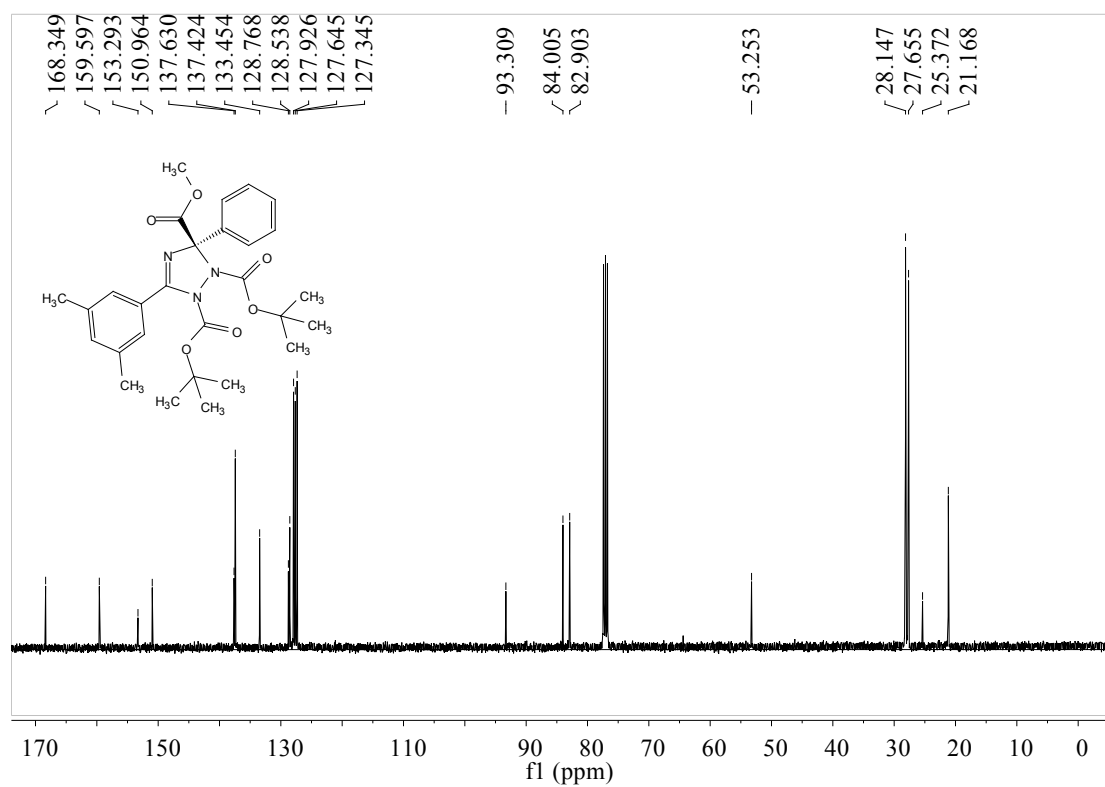
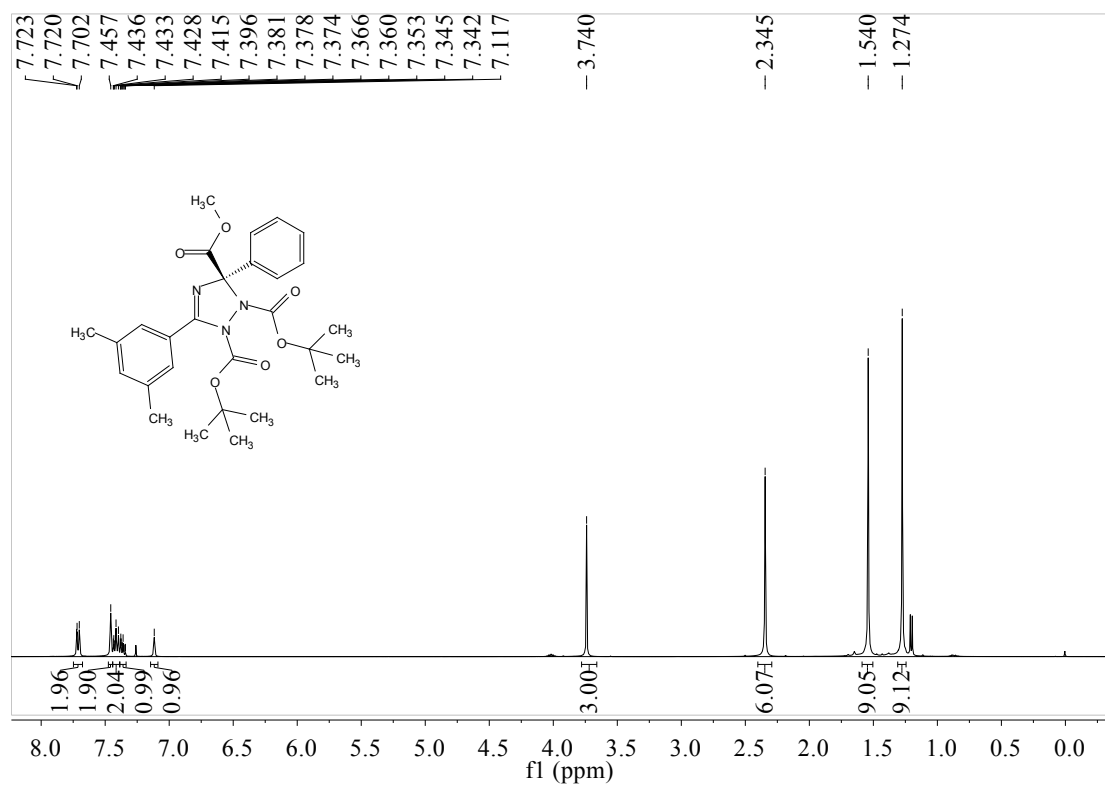
1,2-di-tert-butyl 3-methyl (R)-5-(4-ethoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3cb**)



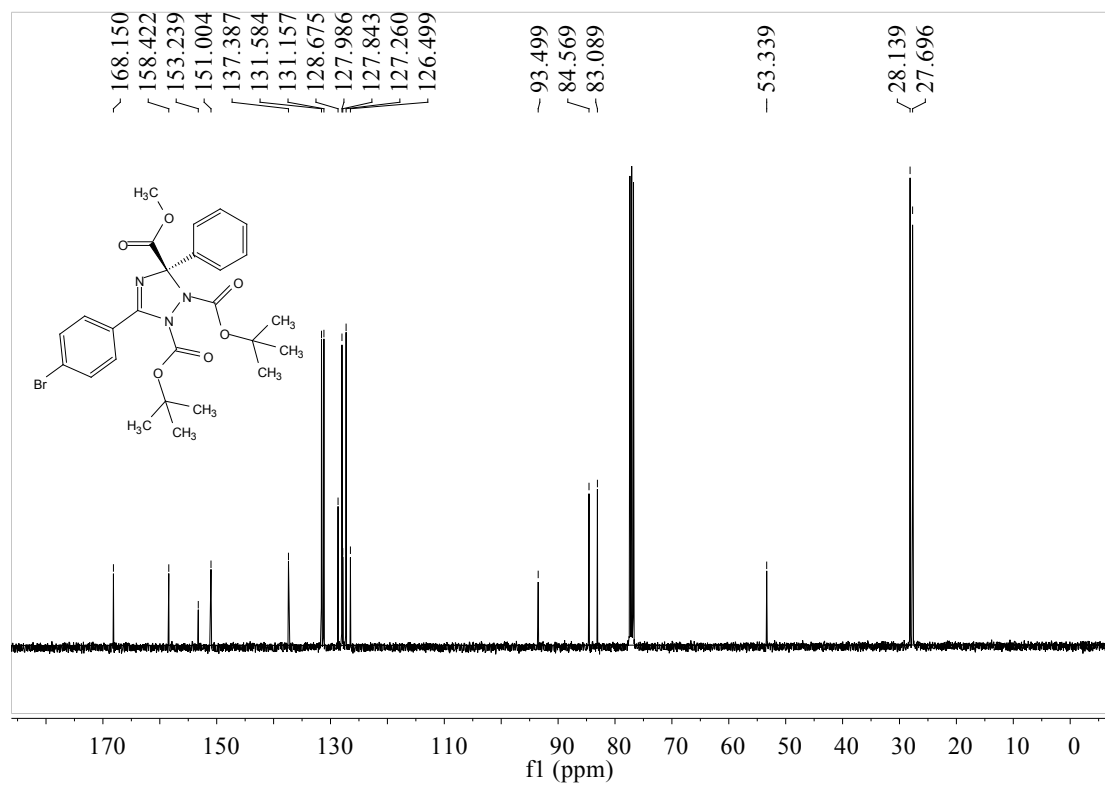
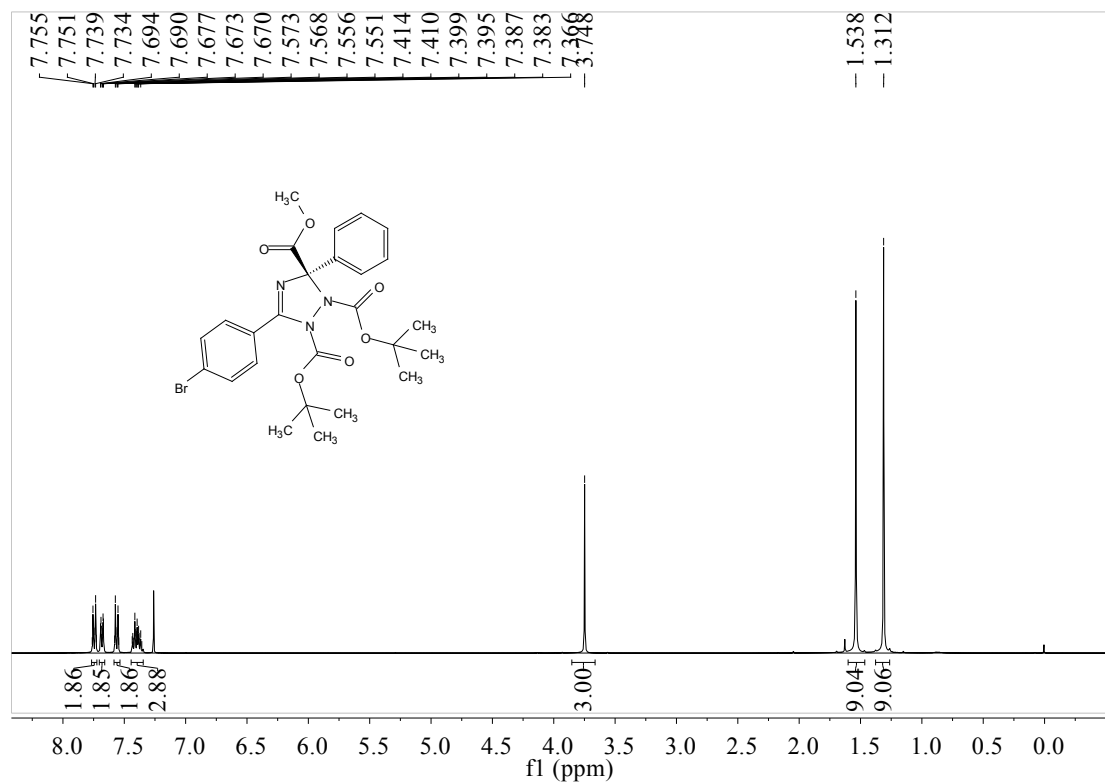
1,2-di-tert-butyl 3-methyl (R)-5-(4-(tert-butyl)phenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(H)-tricarboxylate (**3db**)



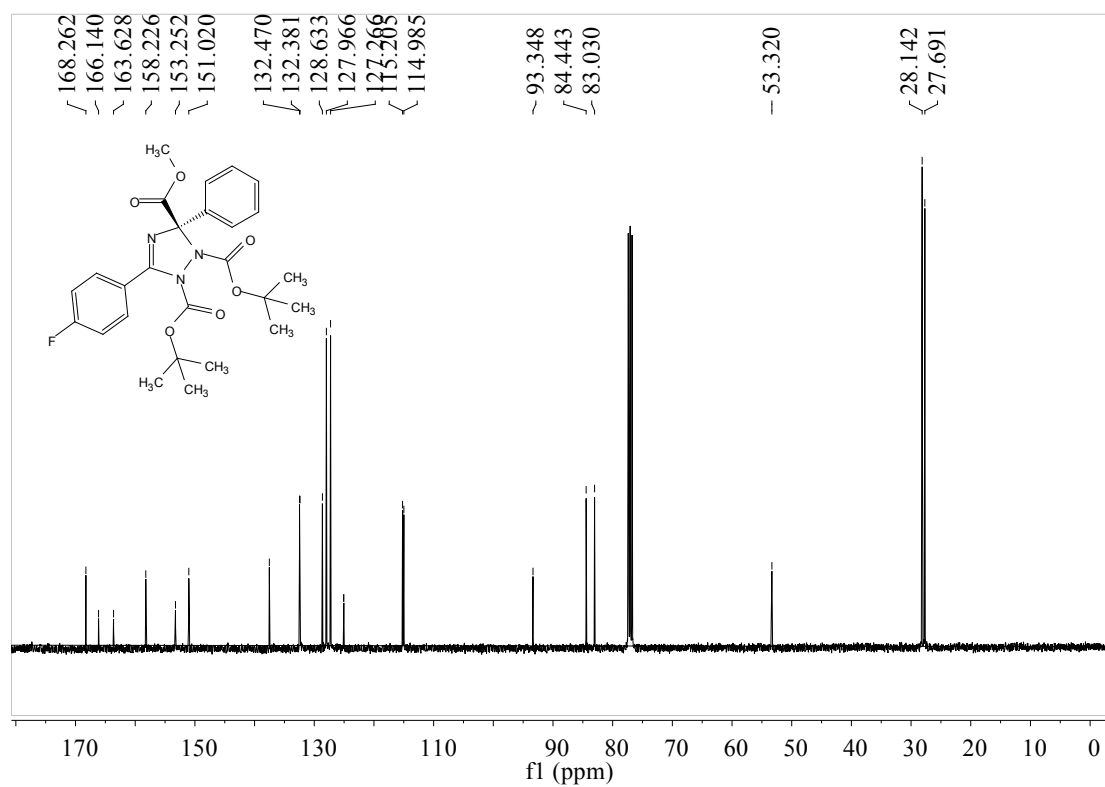
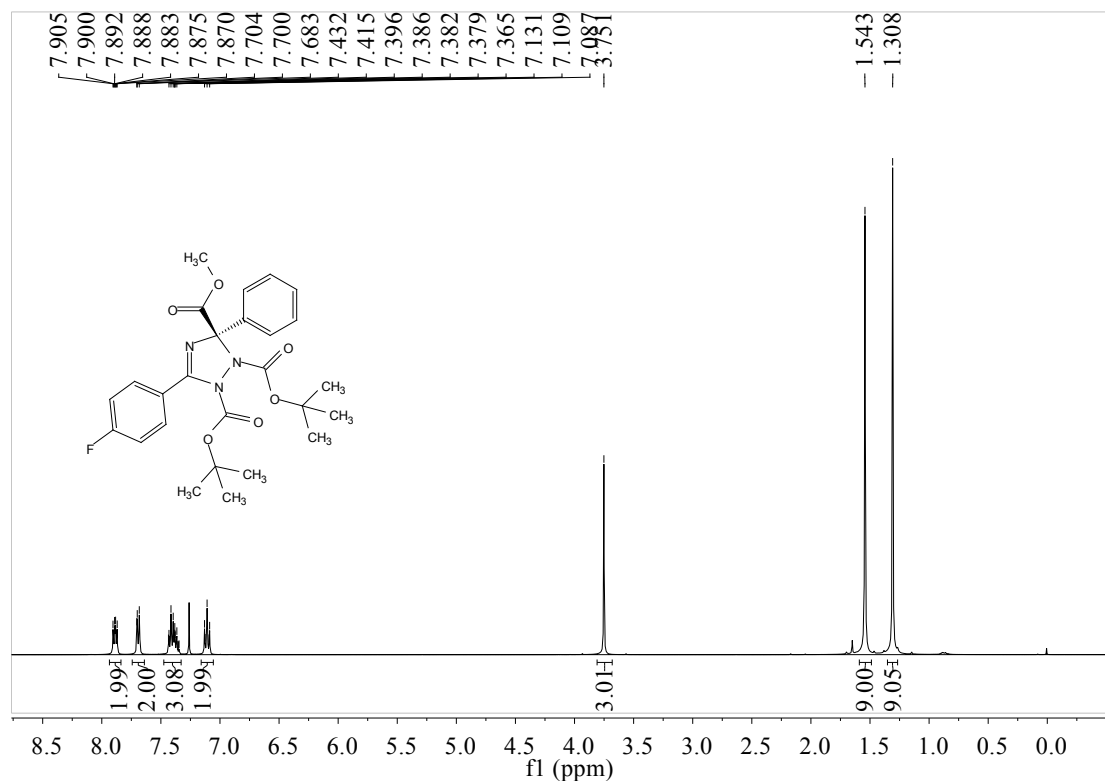
1,2-di-tert-butyl 3-methyl (R)-5-(3,5-dimethylphenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(H)-tricarboxylate (**3eb**)



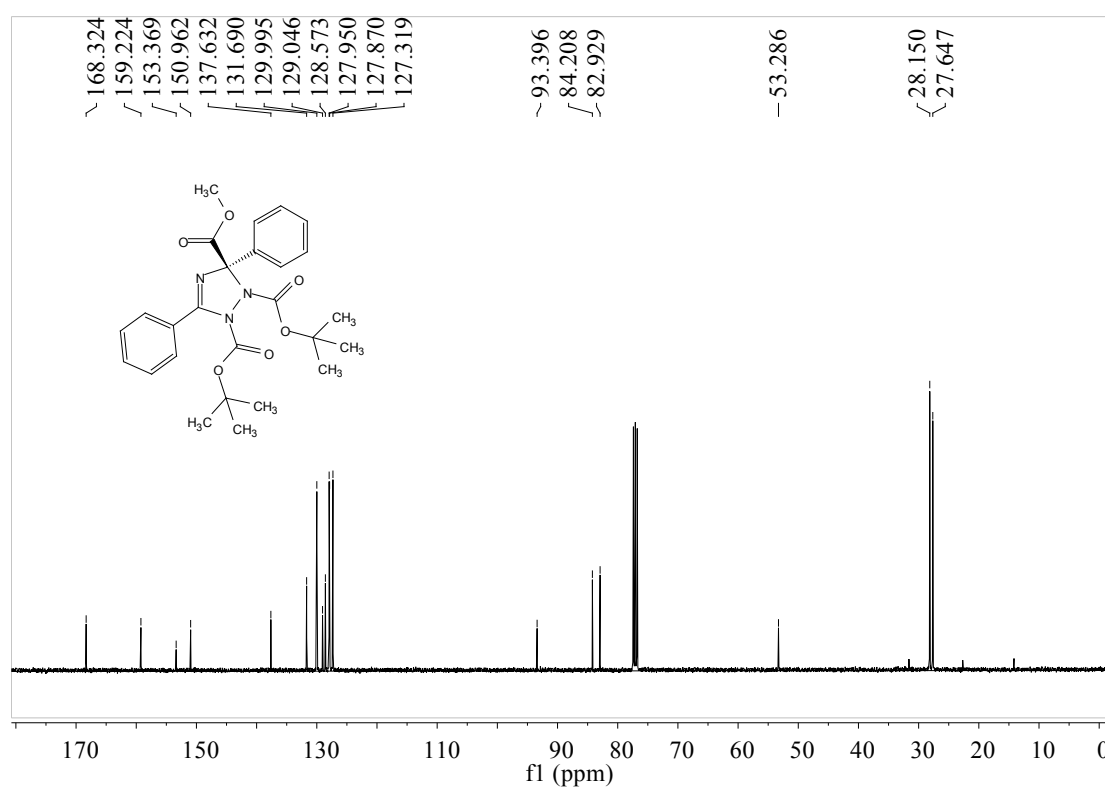
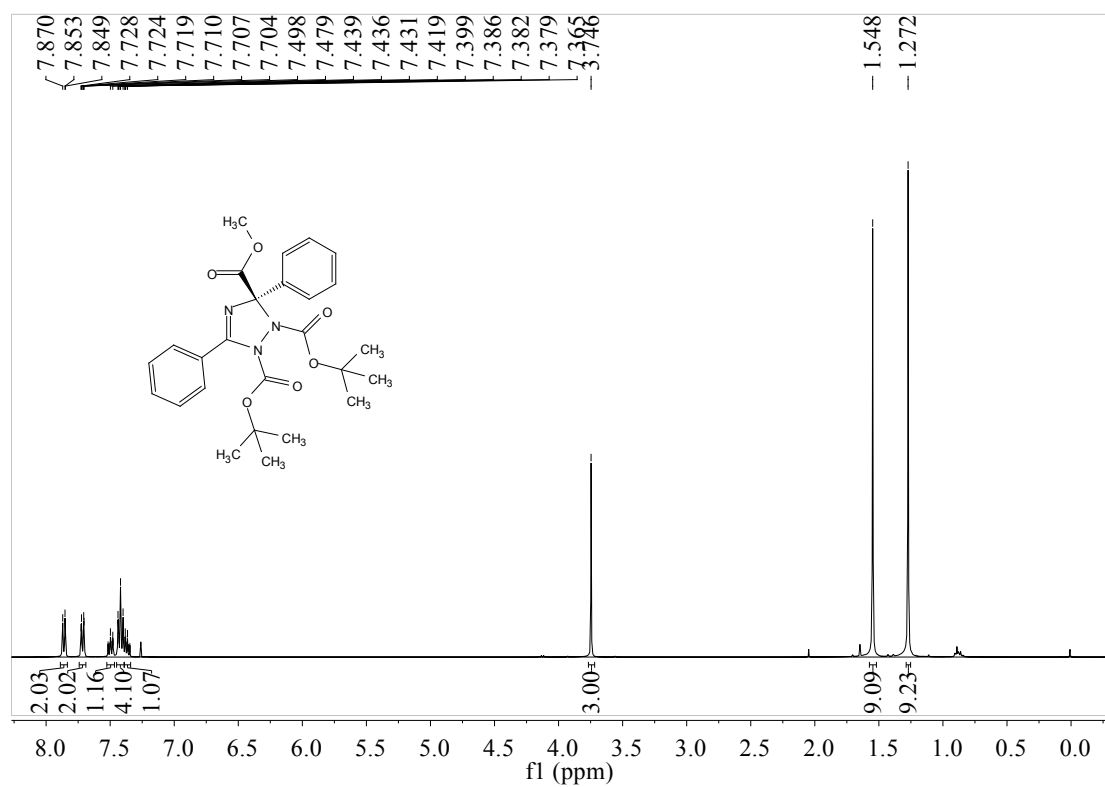
1,2-di-tert-butyl 3-methyl (R)-5-(4-bromophenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3fb**)



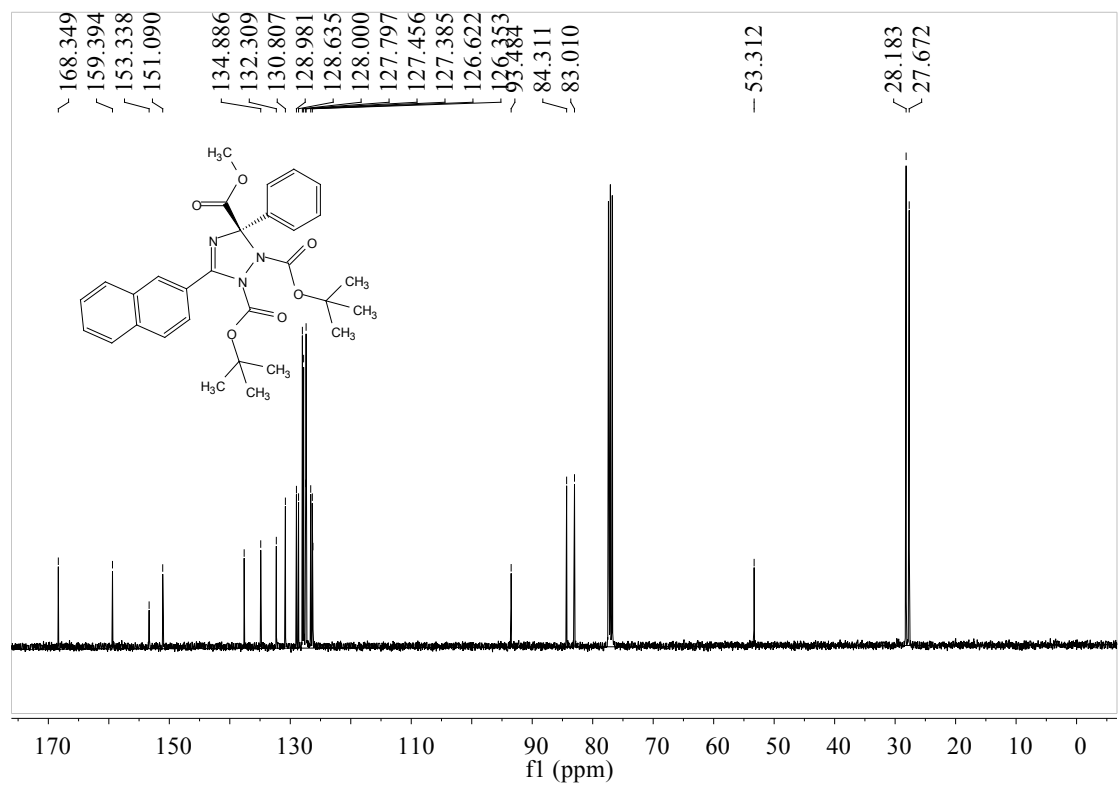
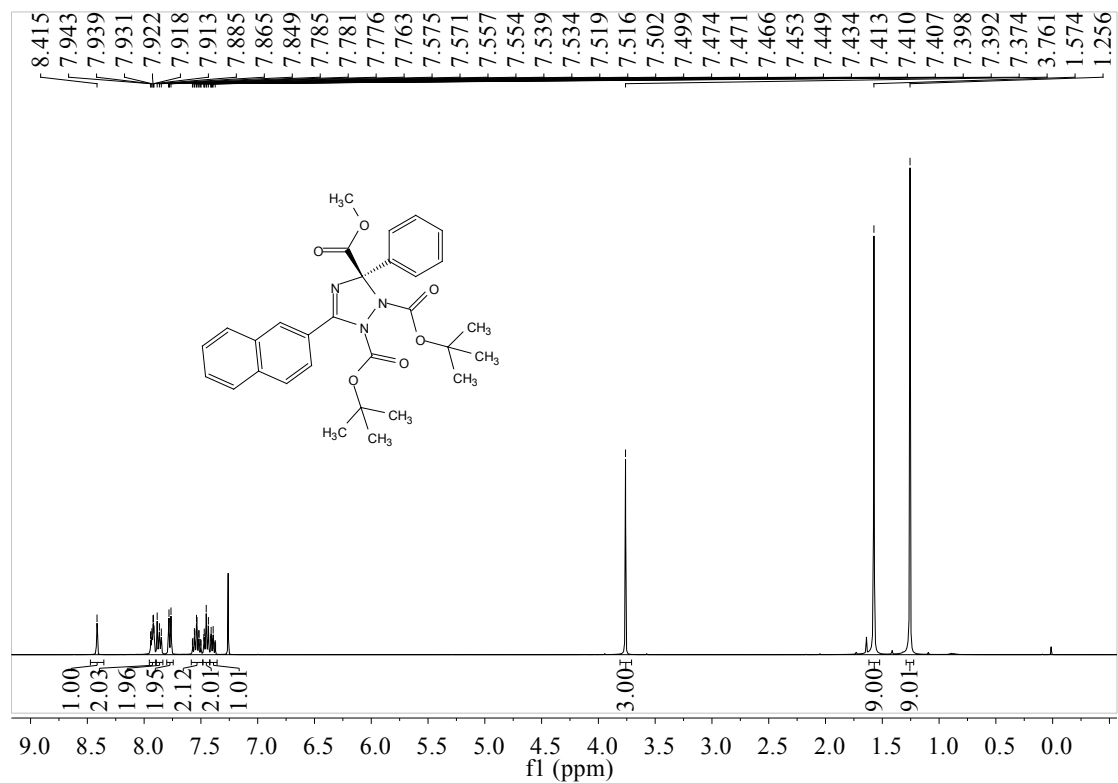
1,2-di-tert-butyl 3-methyl (R)-5-(4-fluorophenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(H)-tricarboxylate (**3gb**)



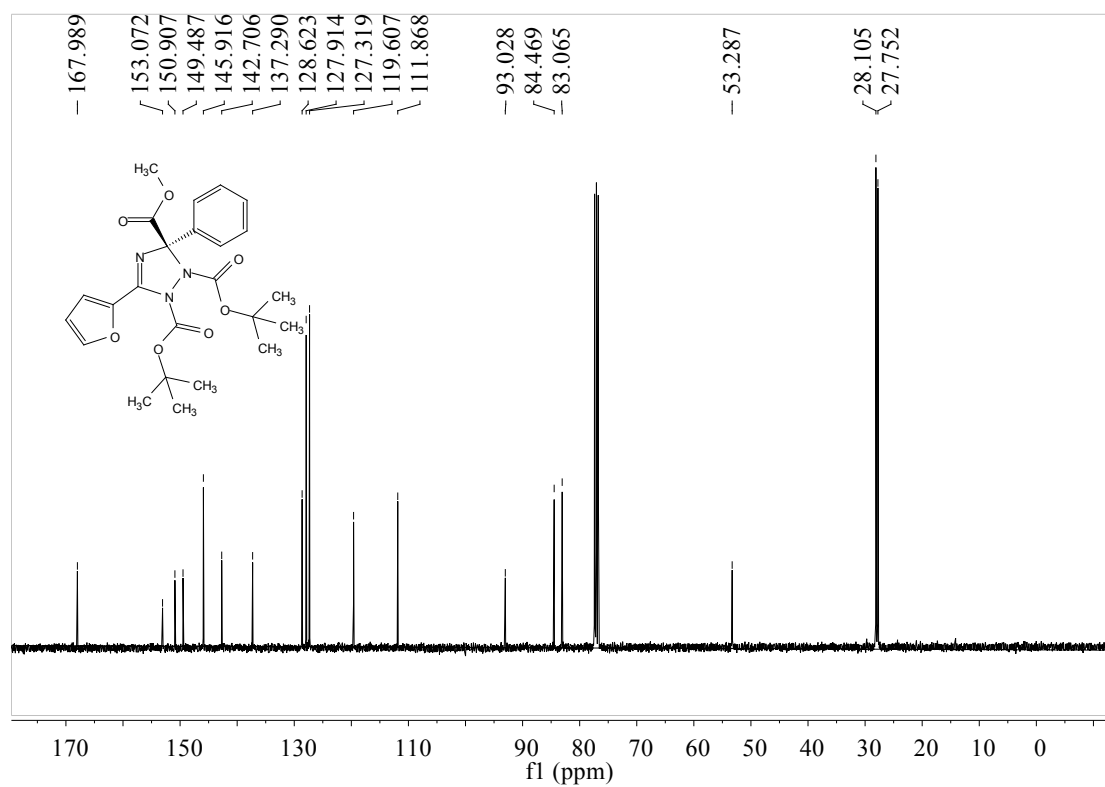
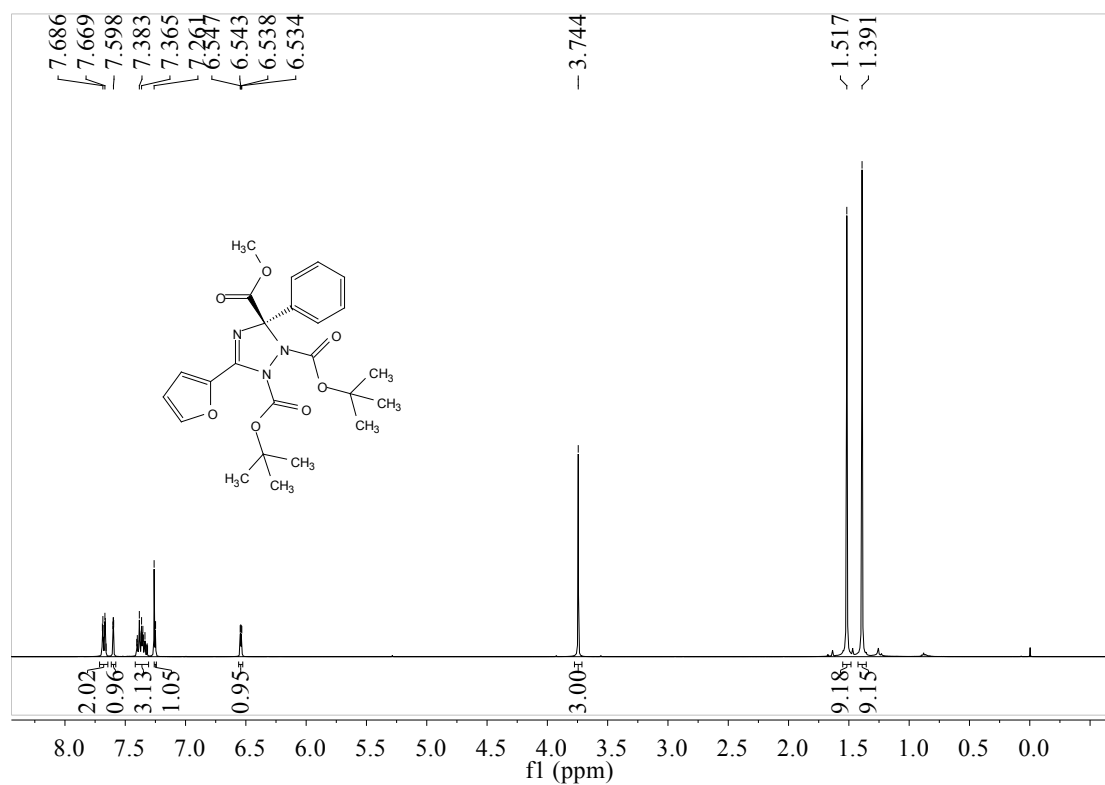
1,2-di-tert-butyl 3-methyl (R)-3,5-diphenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3hb**)



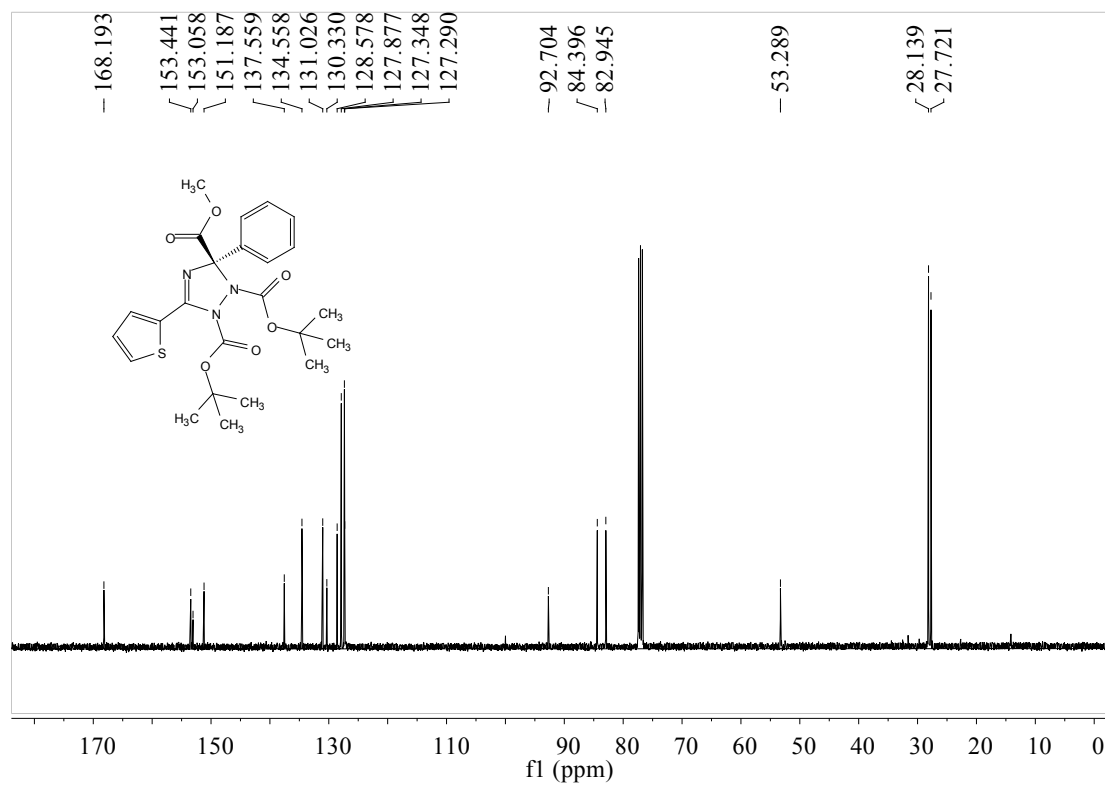
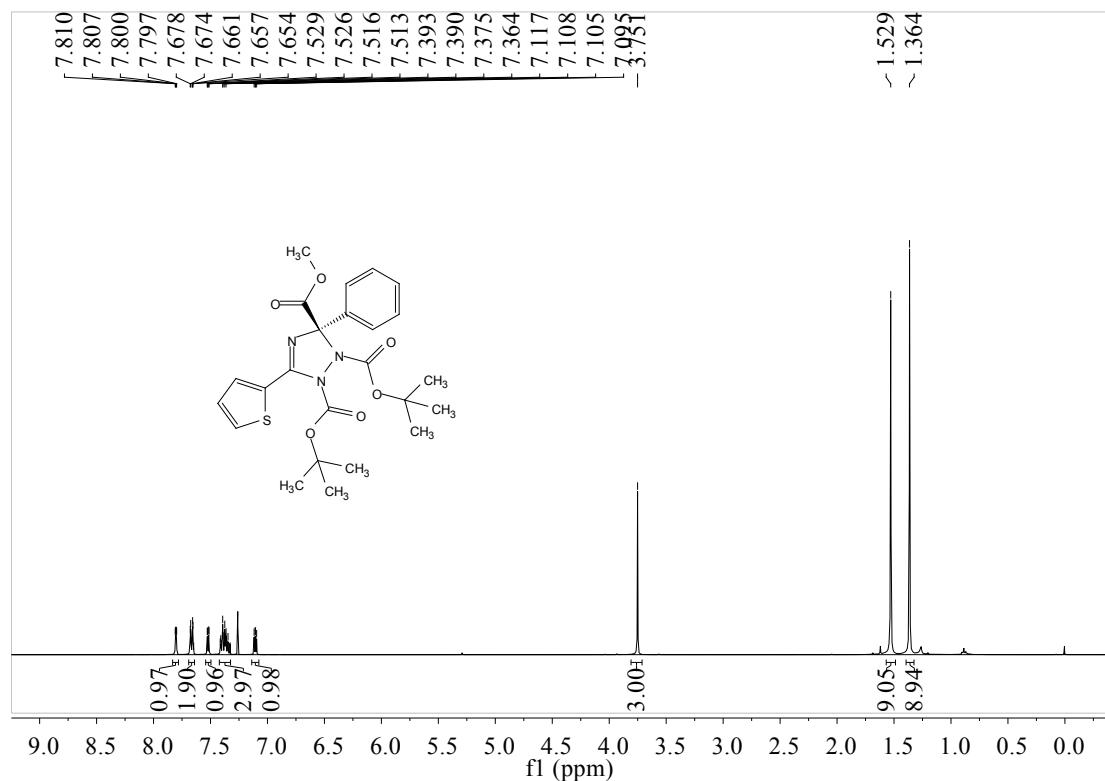
1,2-di-tert-butyl 3-methyl (R)-5-(naphthalen-2-yl)-3-phenyl-1H-1,2,4-triazole-1,2,3(H)-tricarboxylate (**3ib**)



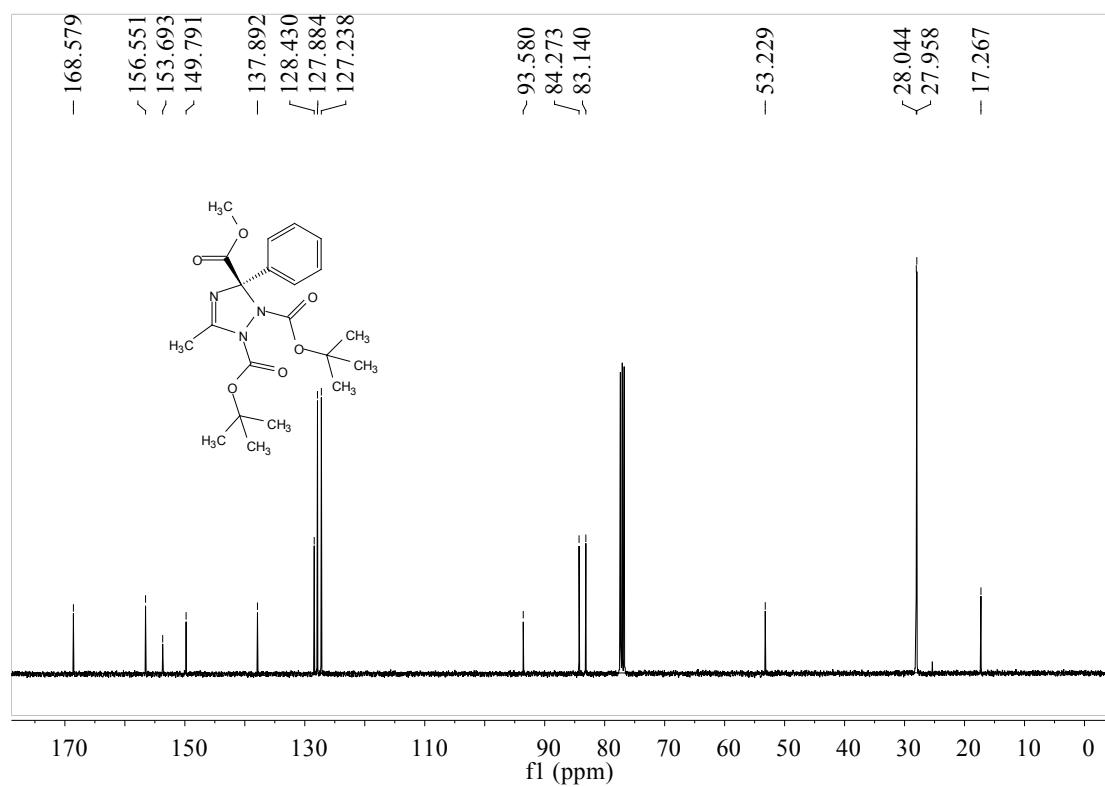
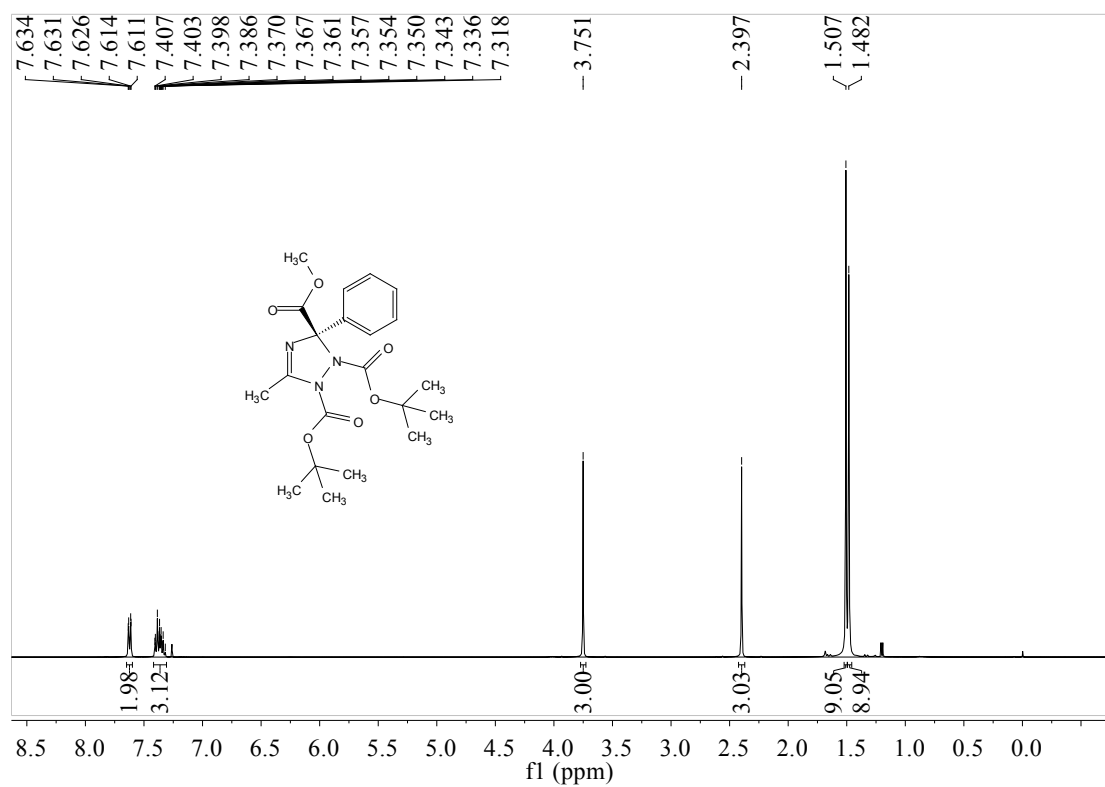
1,2-di-tert-butyl 3-methyl (R)-5-(furan-2-yl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate
(3jb)



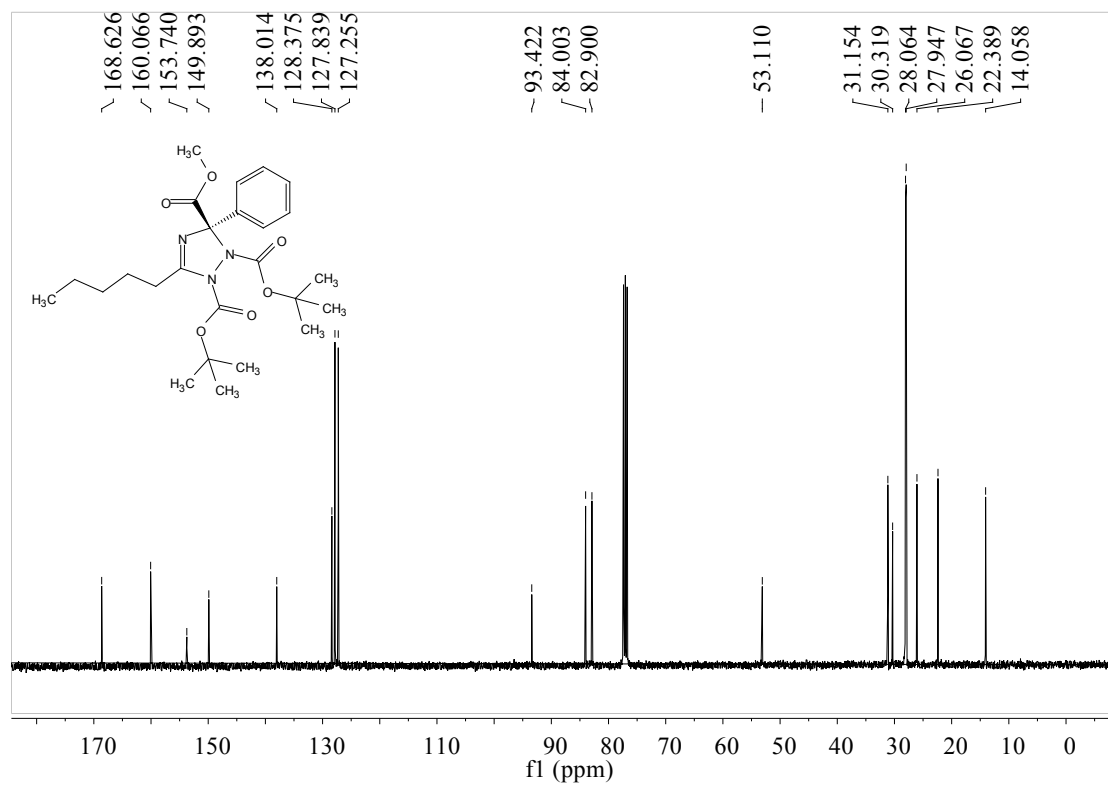
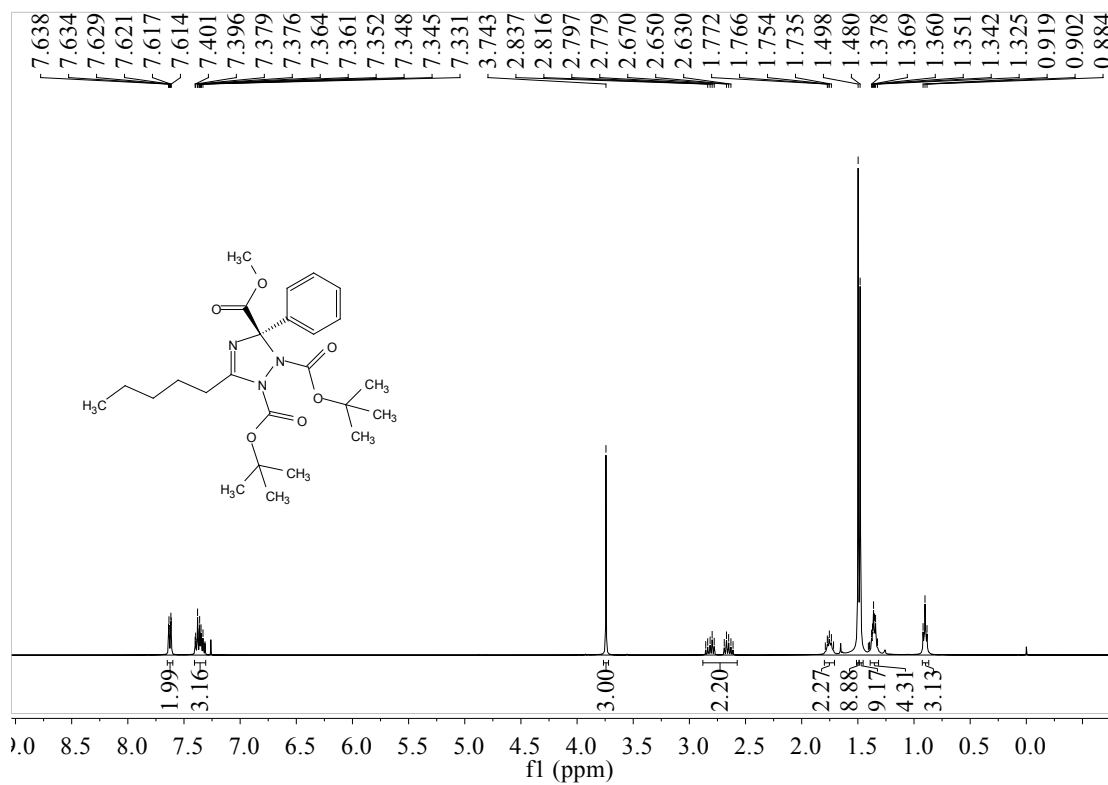
1,2-di-tert-butyl 3-methyl (R)-3-phenyl-5-(thiophen-2-yl)-1H-1,2,4-triazole-1,2,3(H)-tricarboxylate (**3kb**)



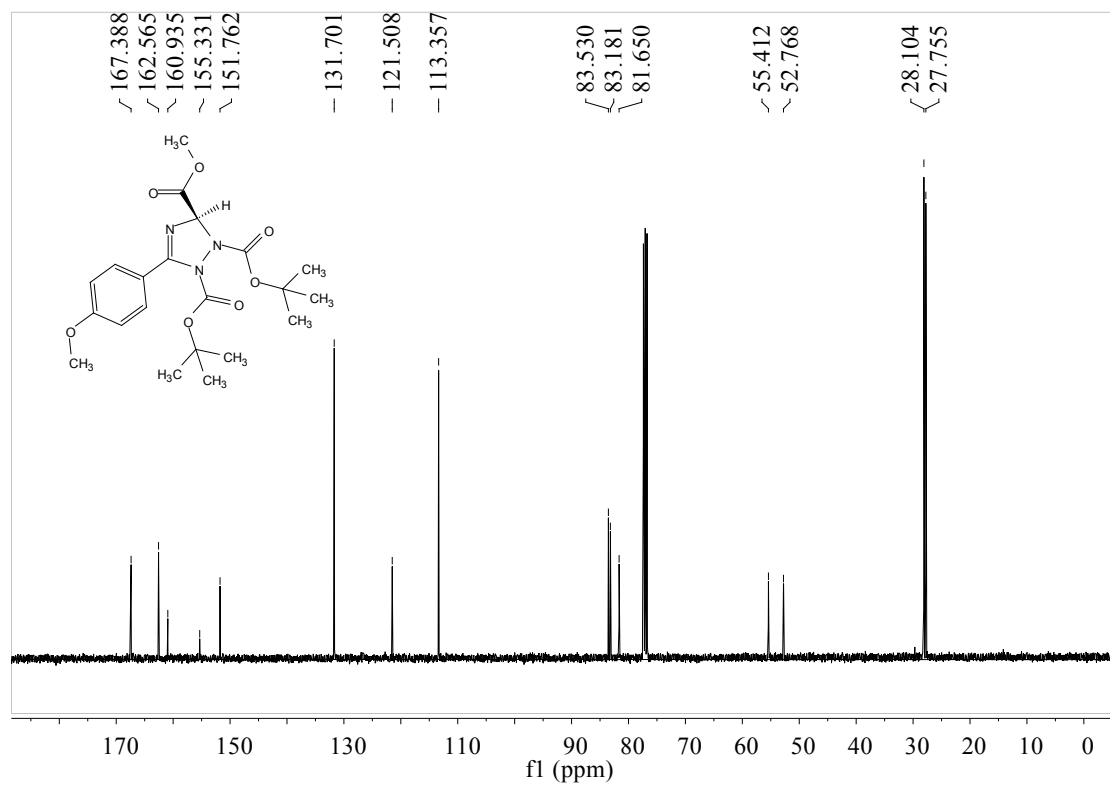
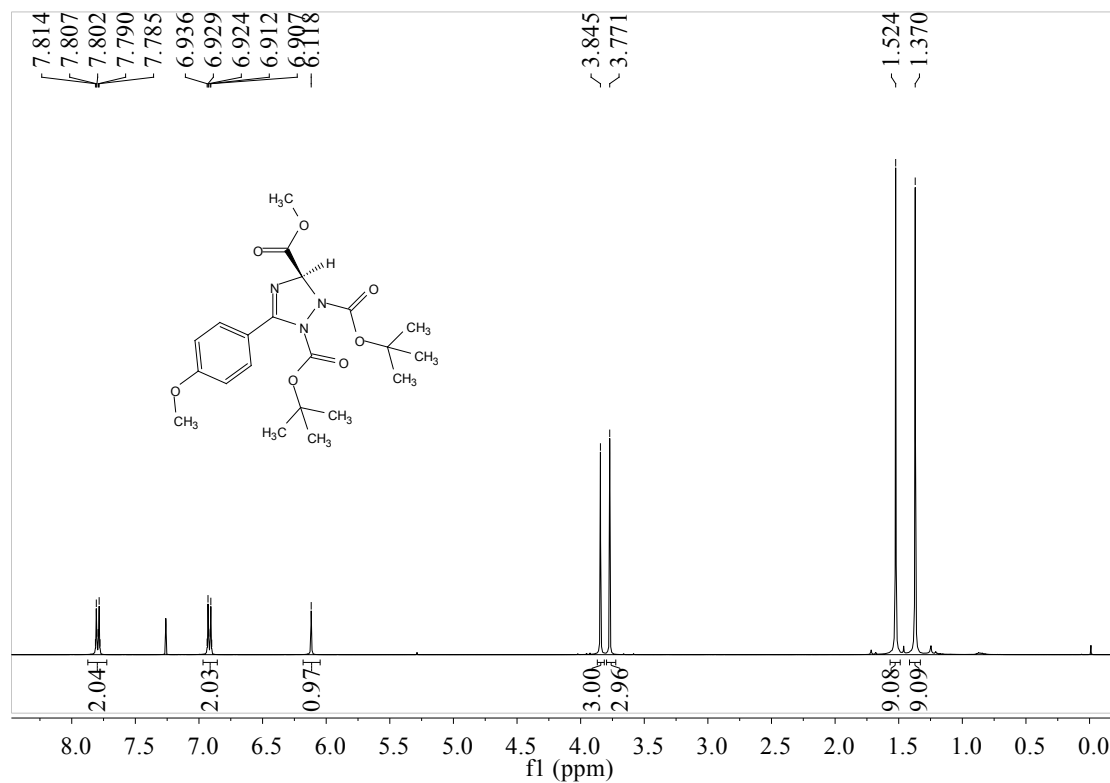
1,2-di-tert-butyl 3-methyl (R)-5-methyl-3-phenyl-1H-1,2,4-triazole-1,2,3(H)-tricarboxylate (**31b**)



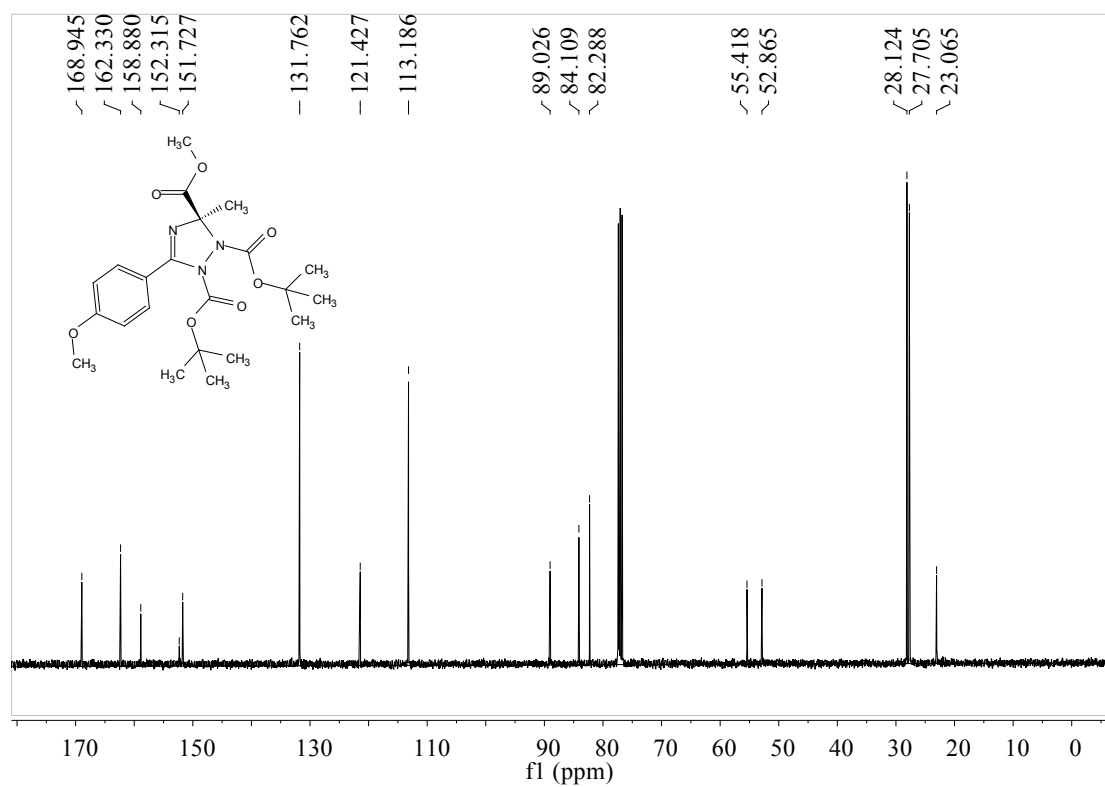
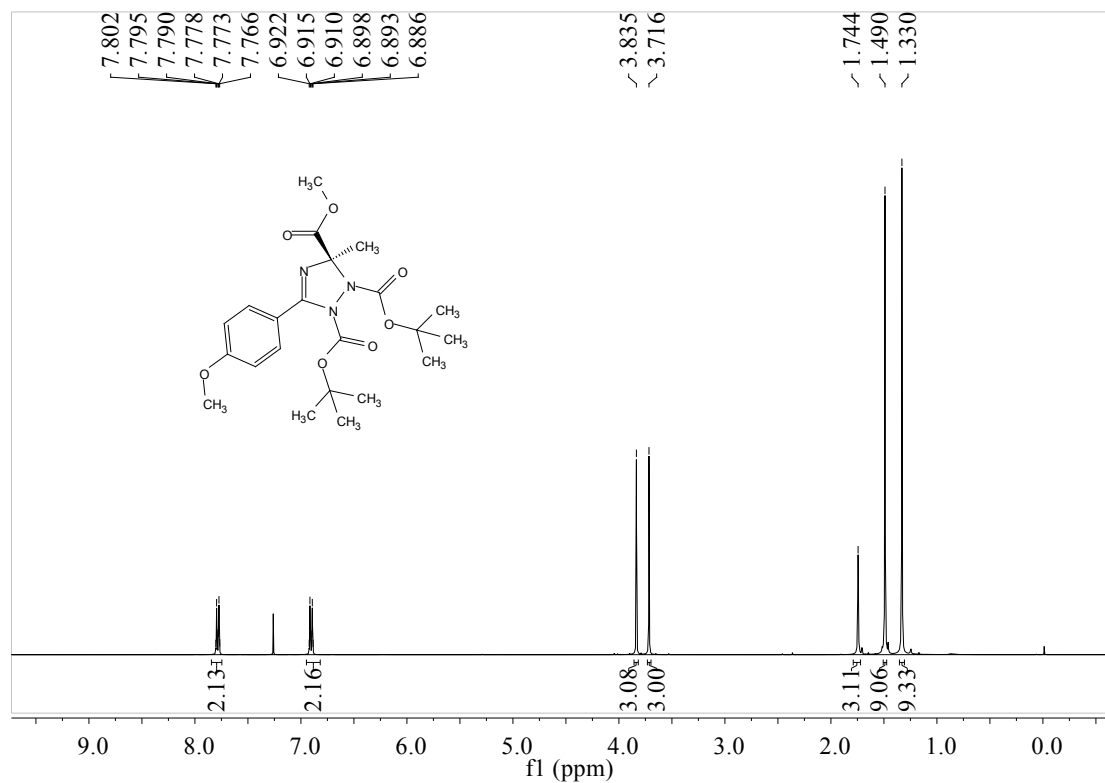
1,2-di-tert-butyl 3-methyl (R)-5-pentyl-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3mb**)



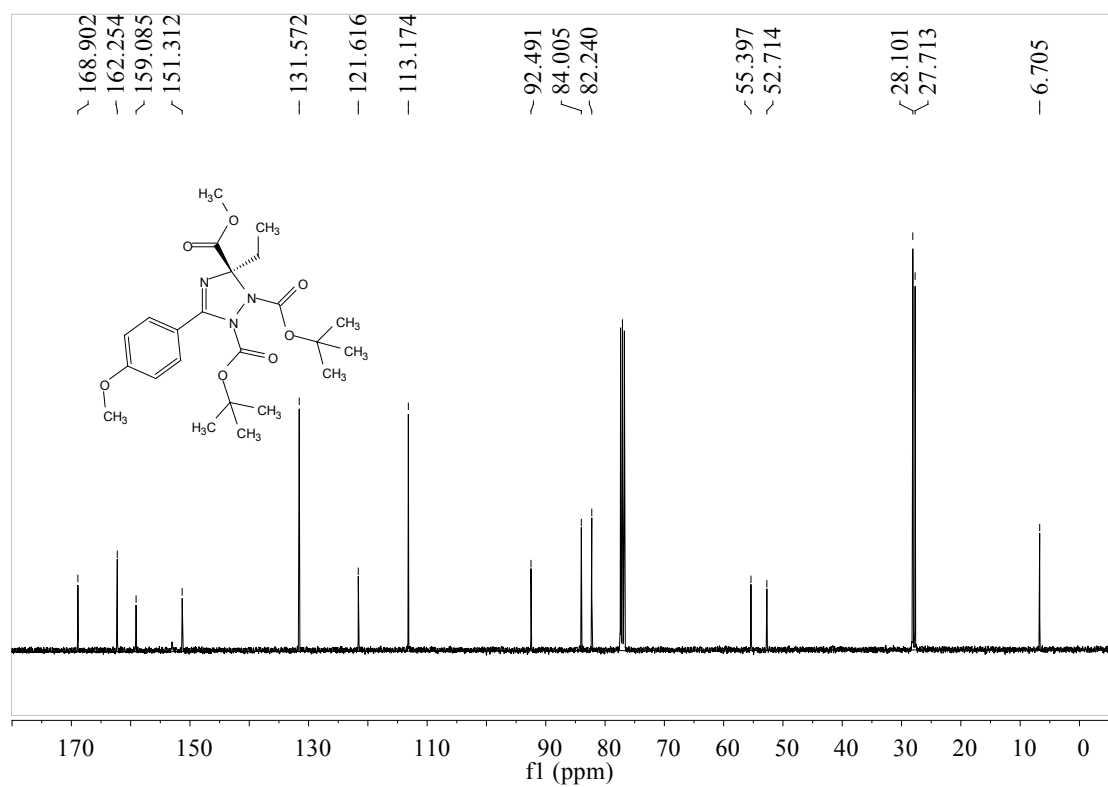
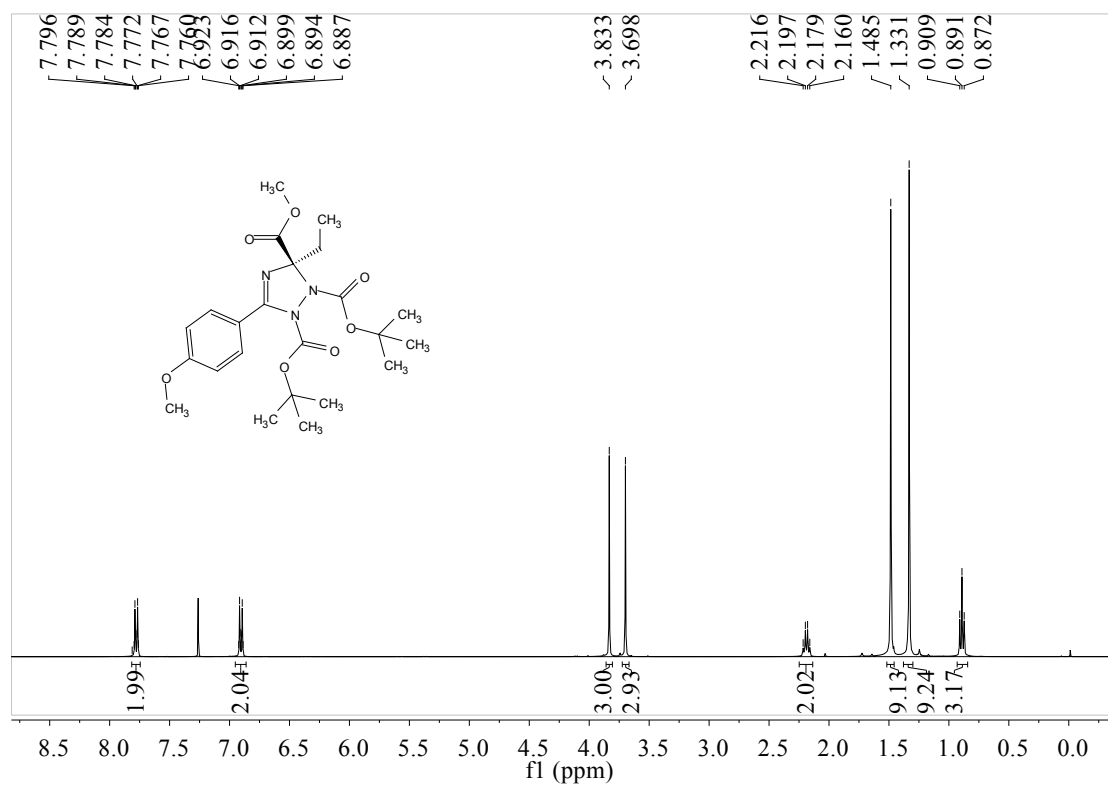
1,2-di-tert-butyl 3-methyl (R)-5-(4-methoxyphenyl)-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate
(3nb)



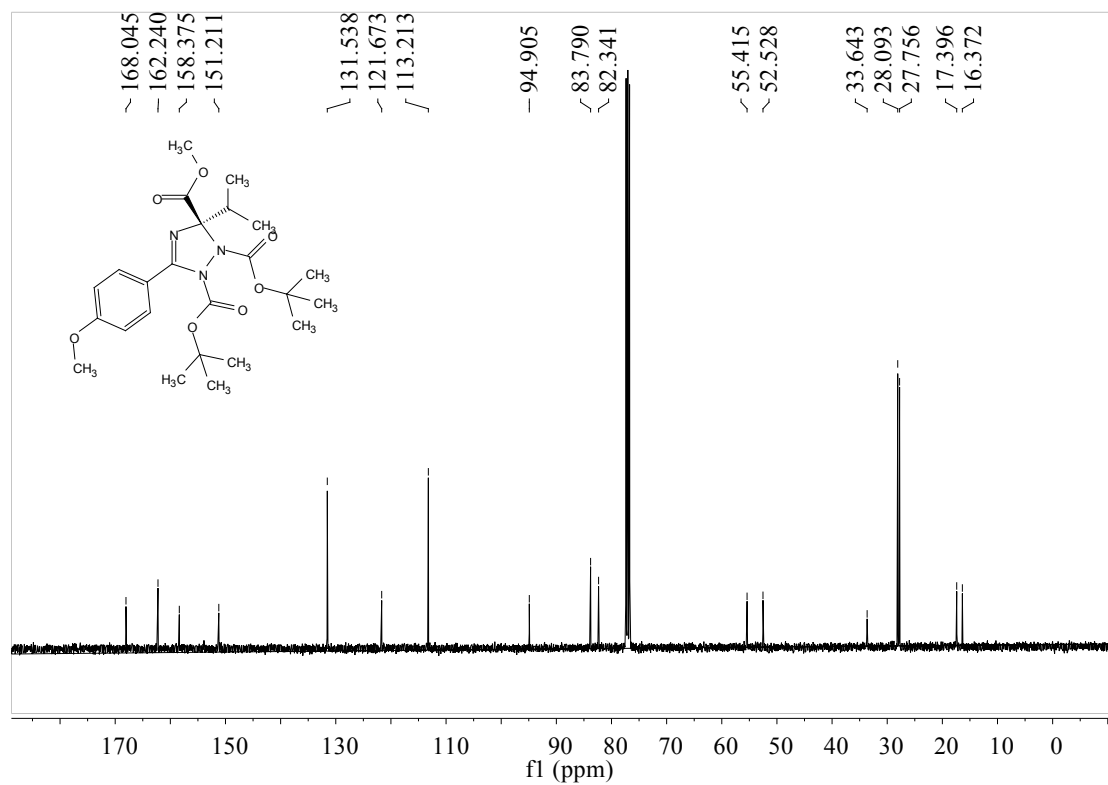
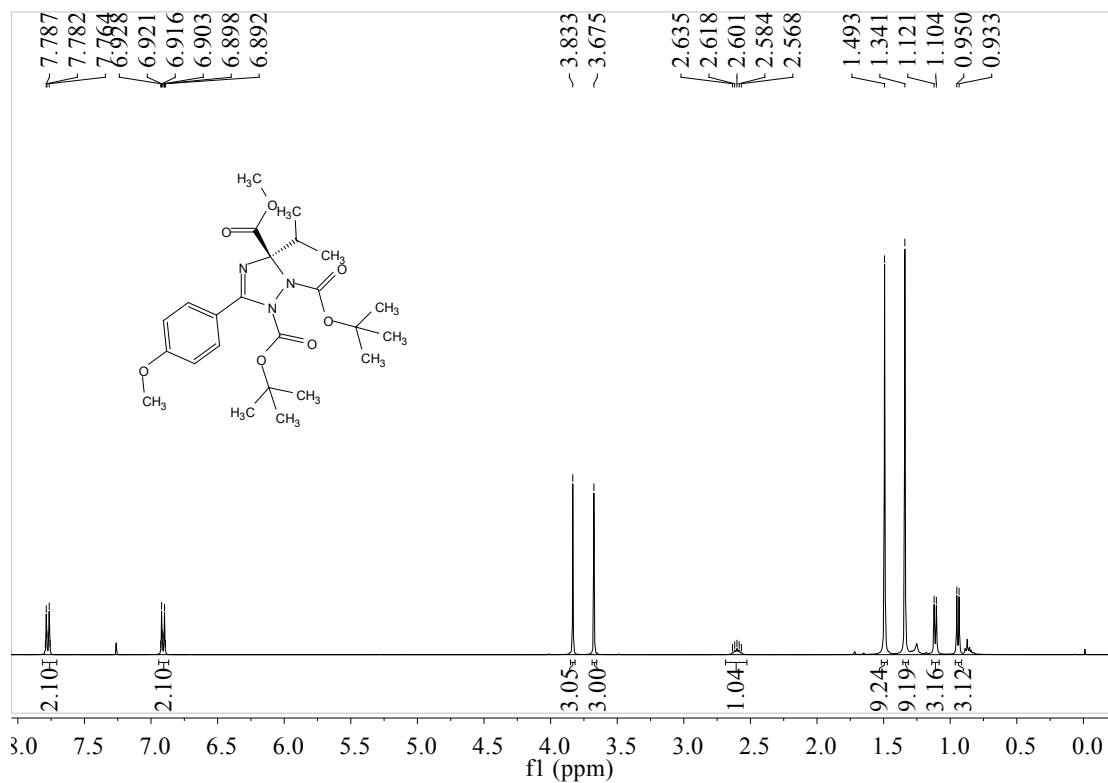
1,2-di-tert-butyl 3-methyl (R)-5-(4-methoxyphenyl)-3-methyl-1H-1,2,4-triazole-1,2,3(H)-tricarboxylate (**3ob**)



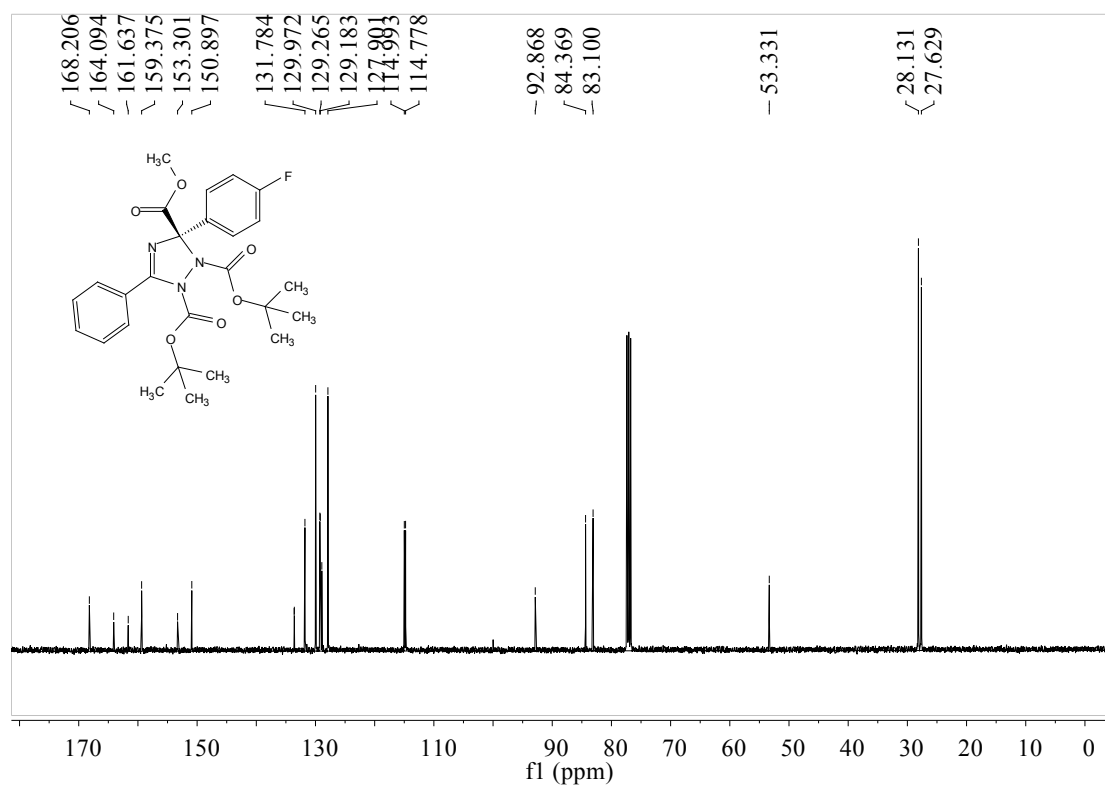
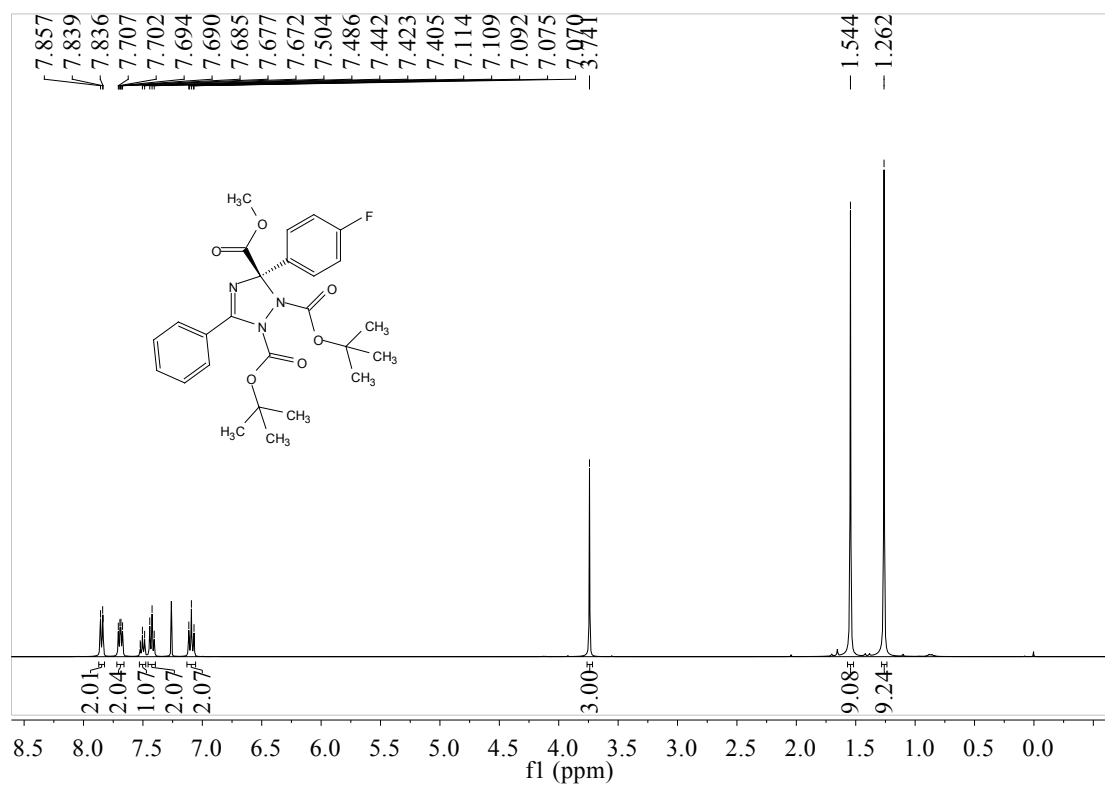
1,2-di-tert-butyl 3-methyl (R)-3-ethyl-5-(4-methoxyphenyl)-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3pb**)



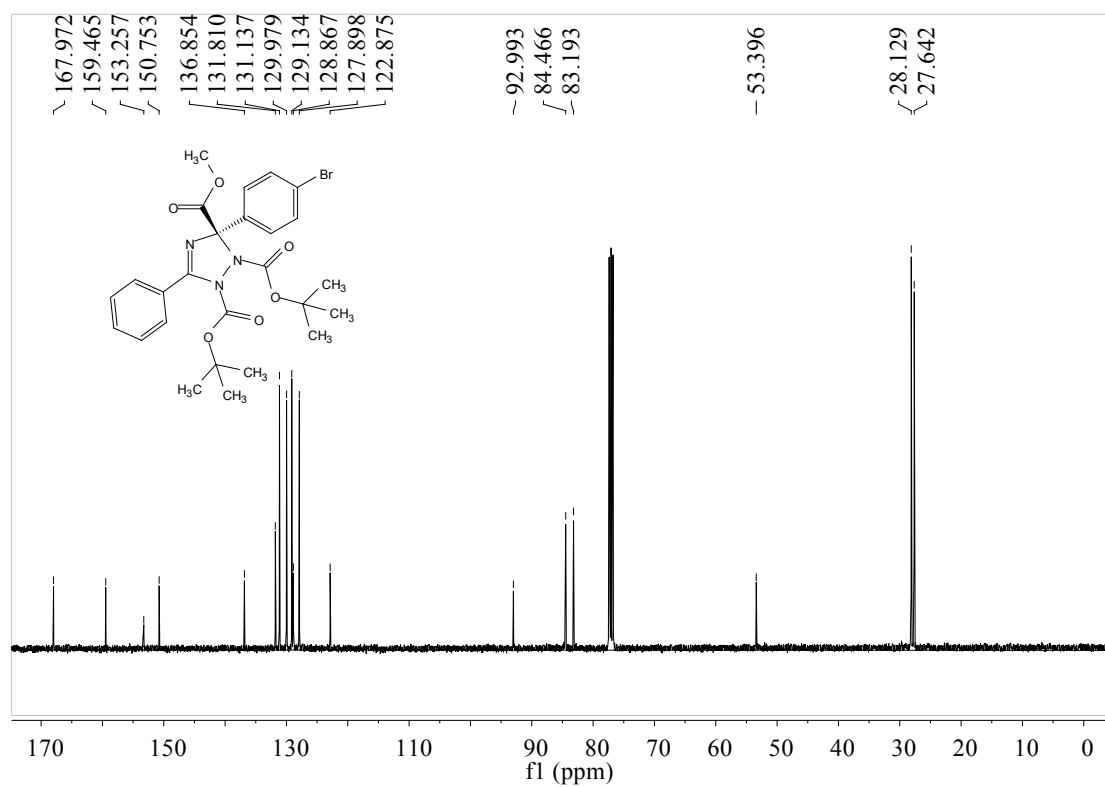
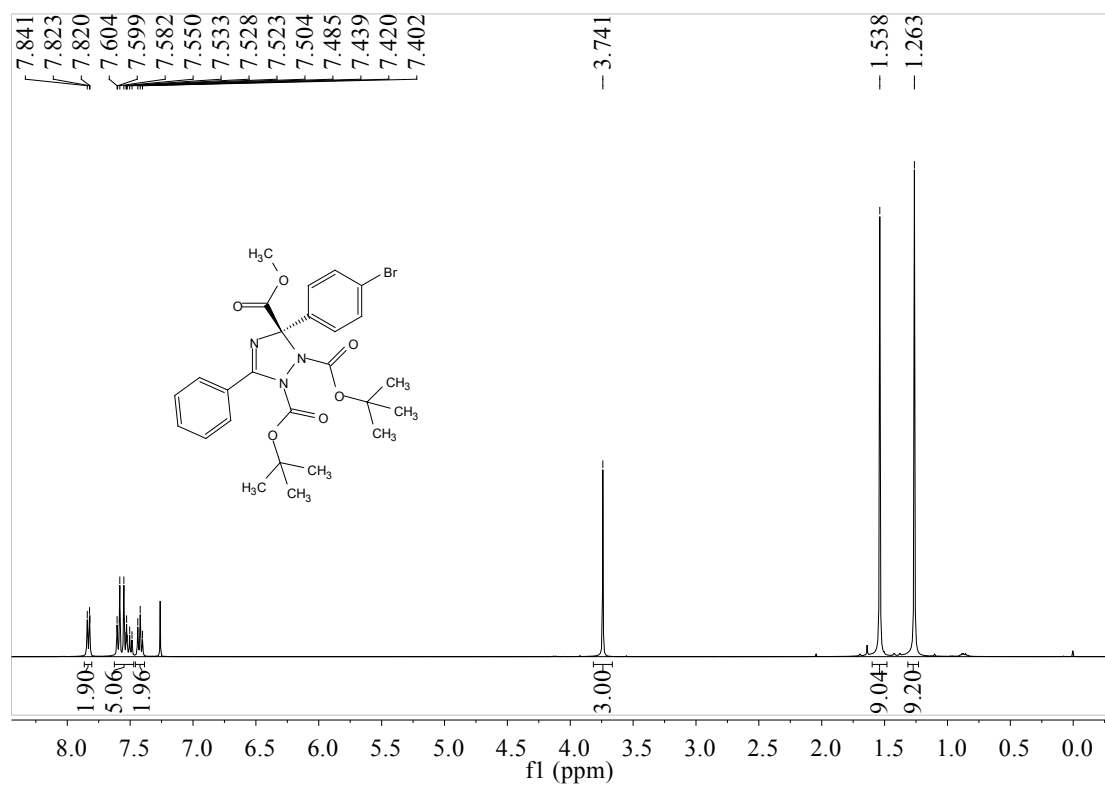
1,2-di-tert-butyl 3-methyl (R)-3-isopropyl-5-(4-methoxyphenyl)-1H-1,2,4-triazole-1,2,3(H)-tricarboxylate (**3qb**)



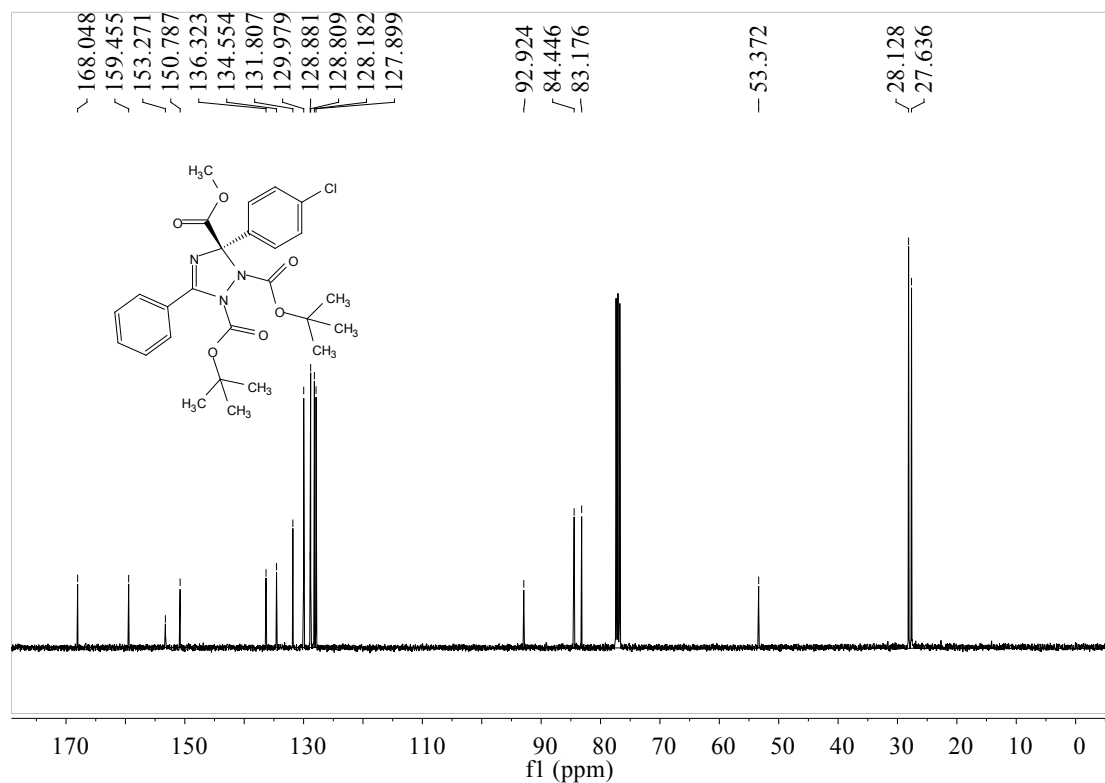
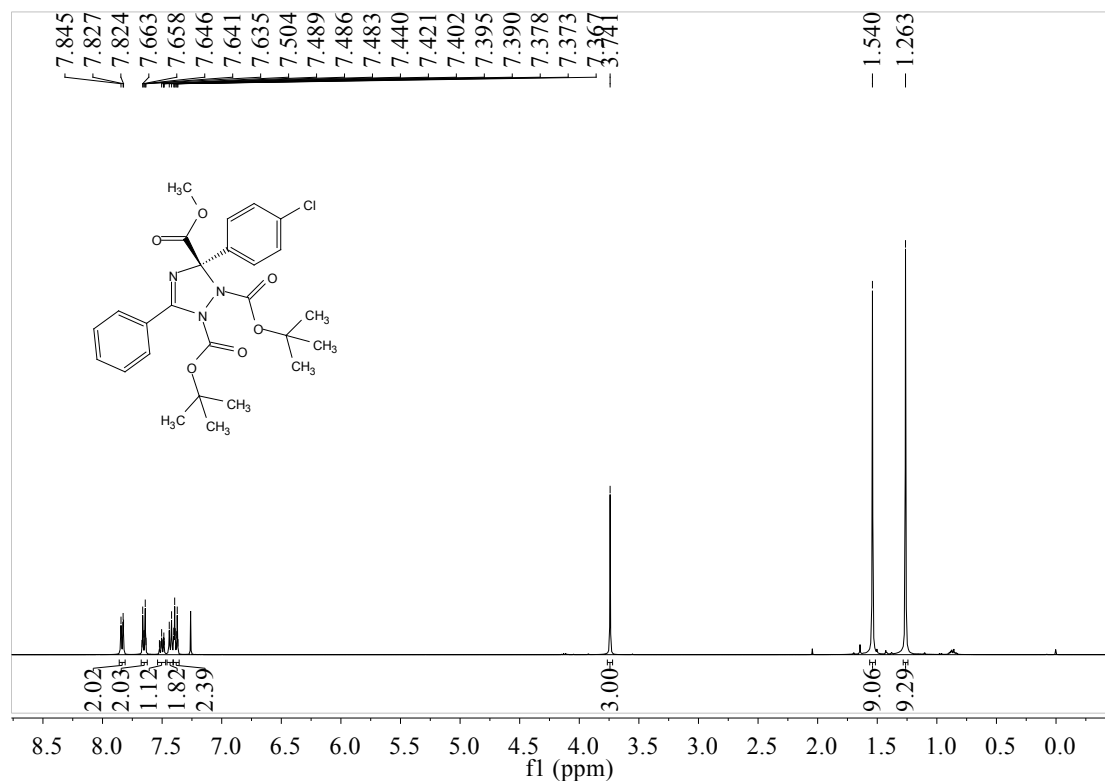
1,2-di-tert-butyl 3-methyl (R)-3-(4-fluorophenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3rb**)



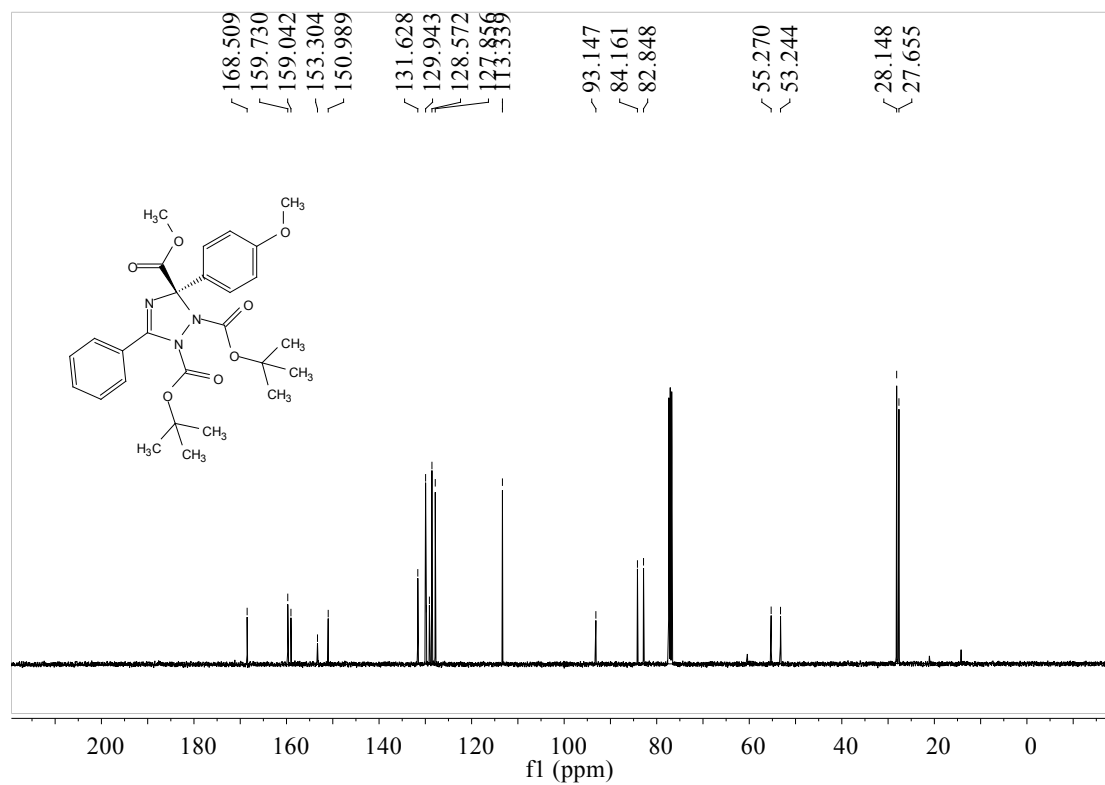
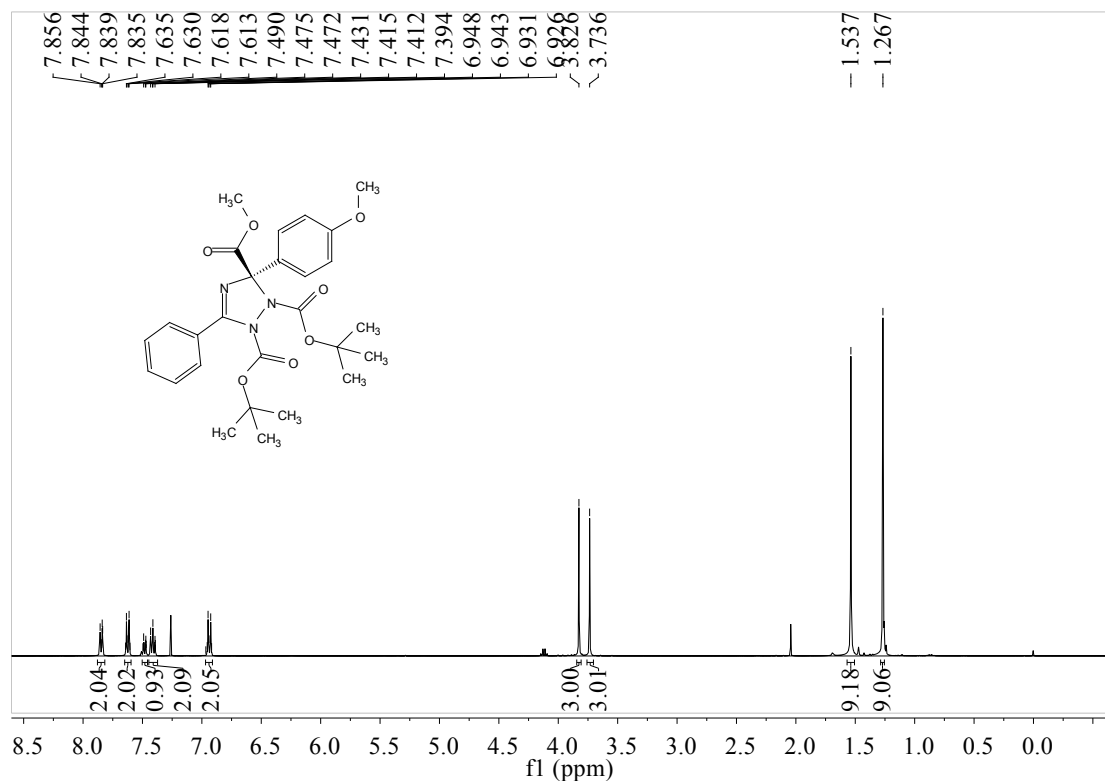
1,2-di-tert-butyl 3-methyl (R)-3-(4-bromophenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(H)-tricarboxylate (**3sb**)



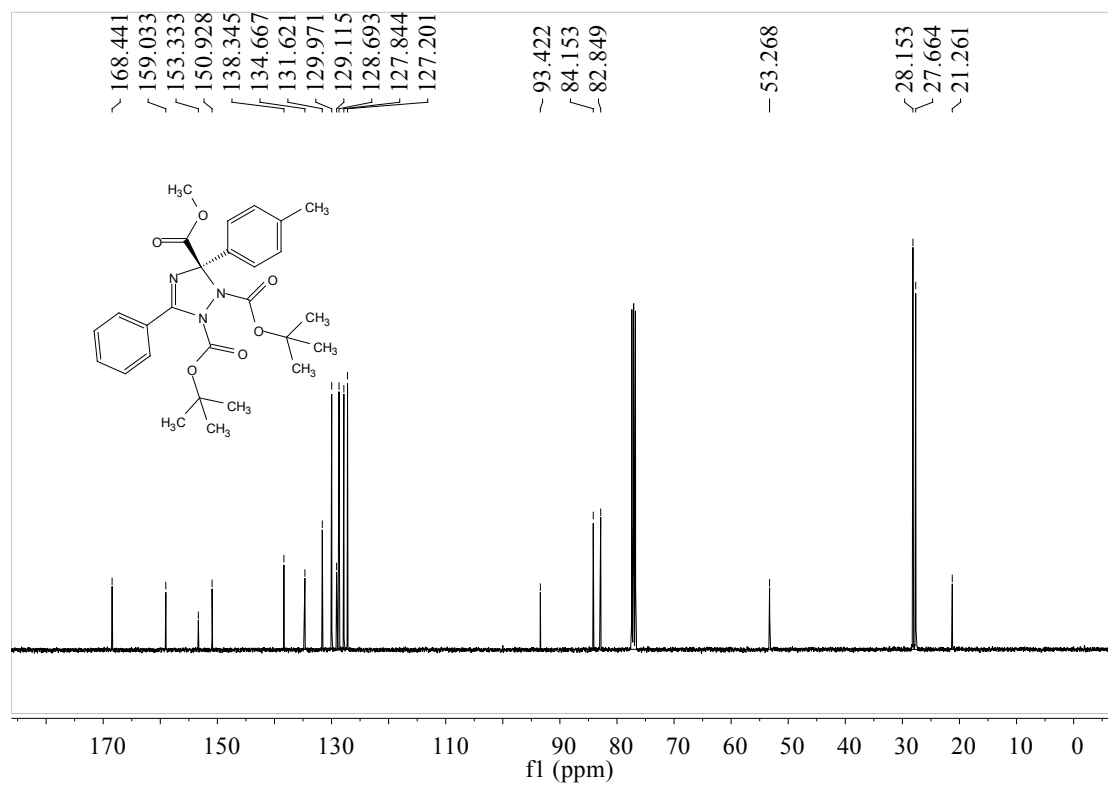
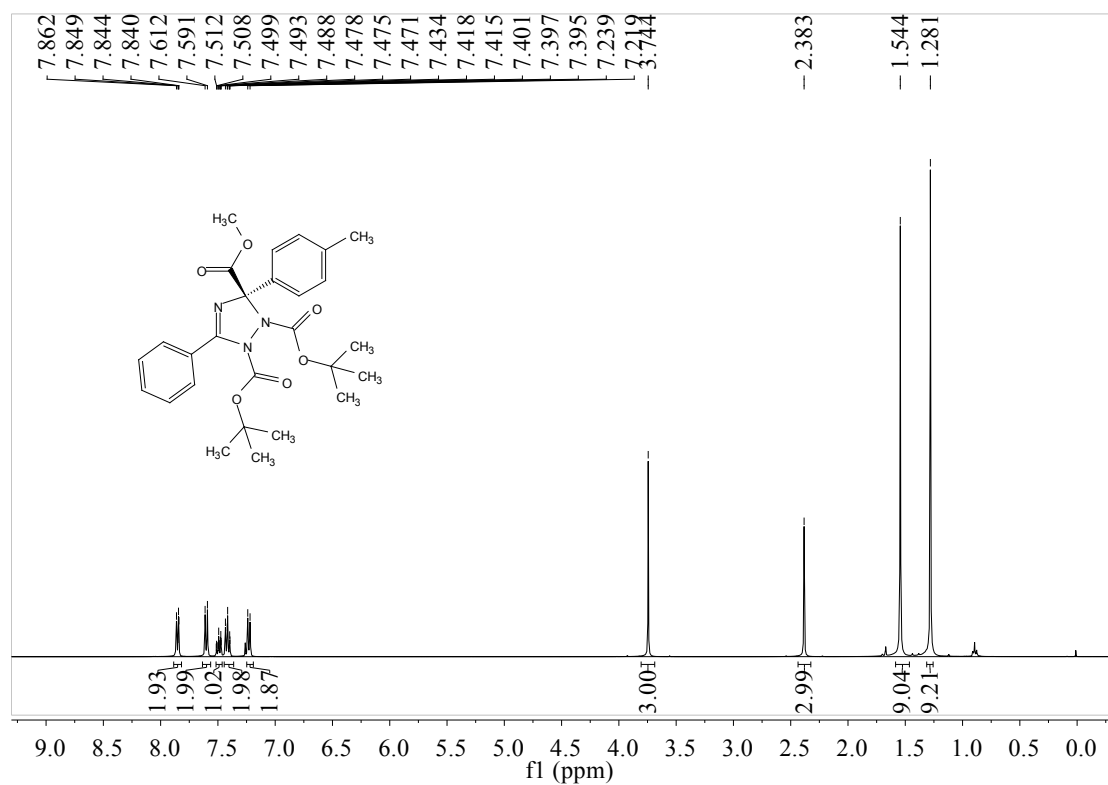
1,2-di-tert-butyl 3-methyl (R)-3-(4-chlorophenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3tb**)



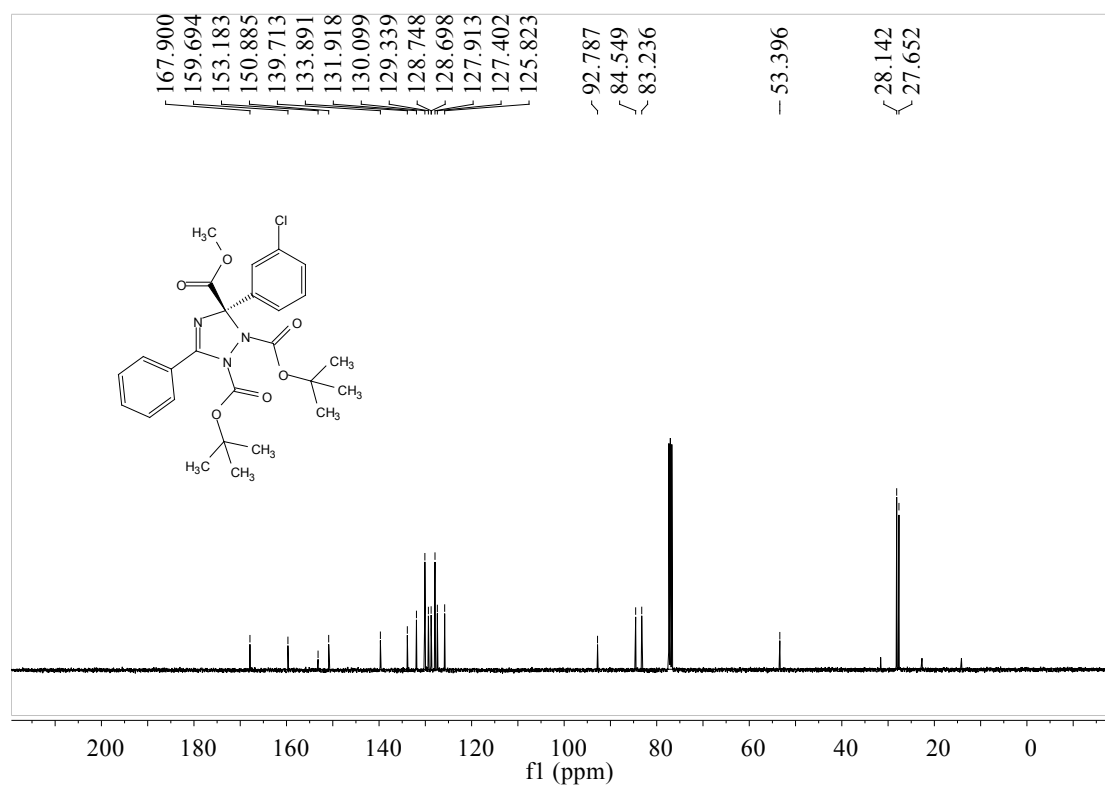
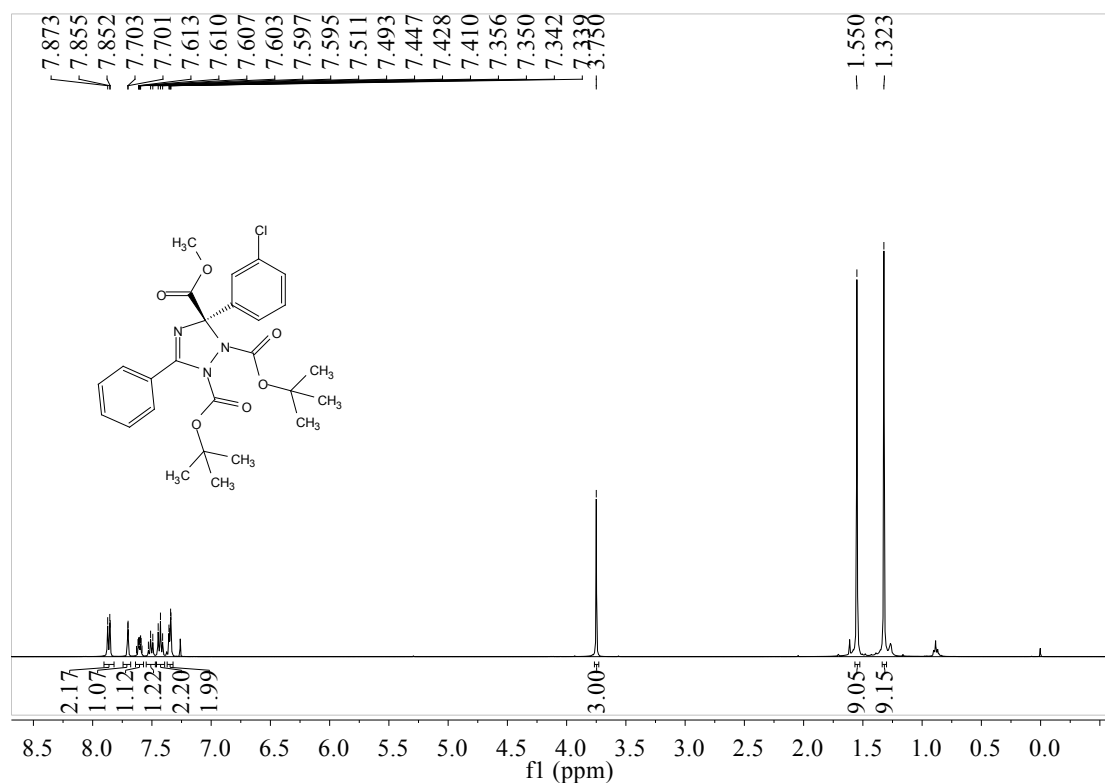
1,2-di-tert-butyl 3-methyl (R)-3-(4-methoxyphenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(H)-tricarboxylate (**3ub**)



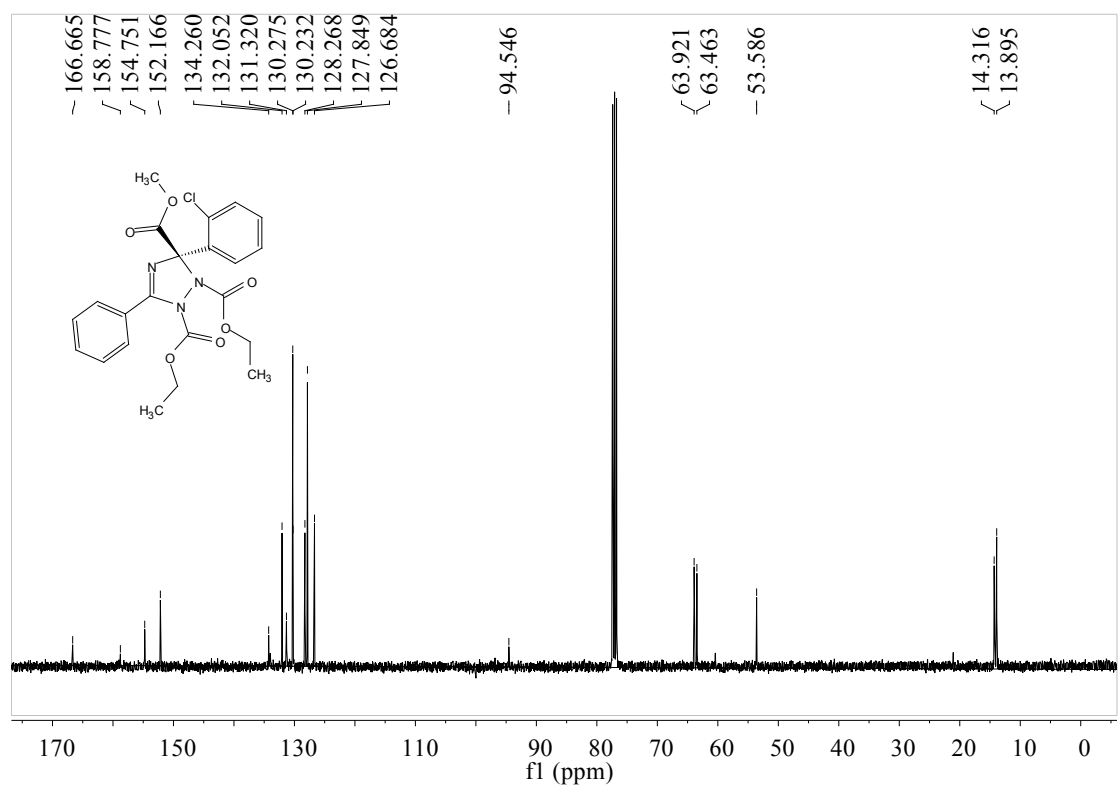
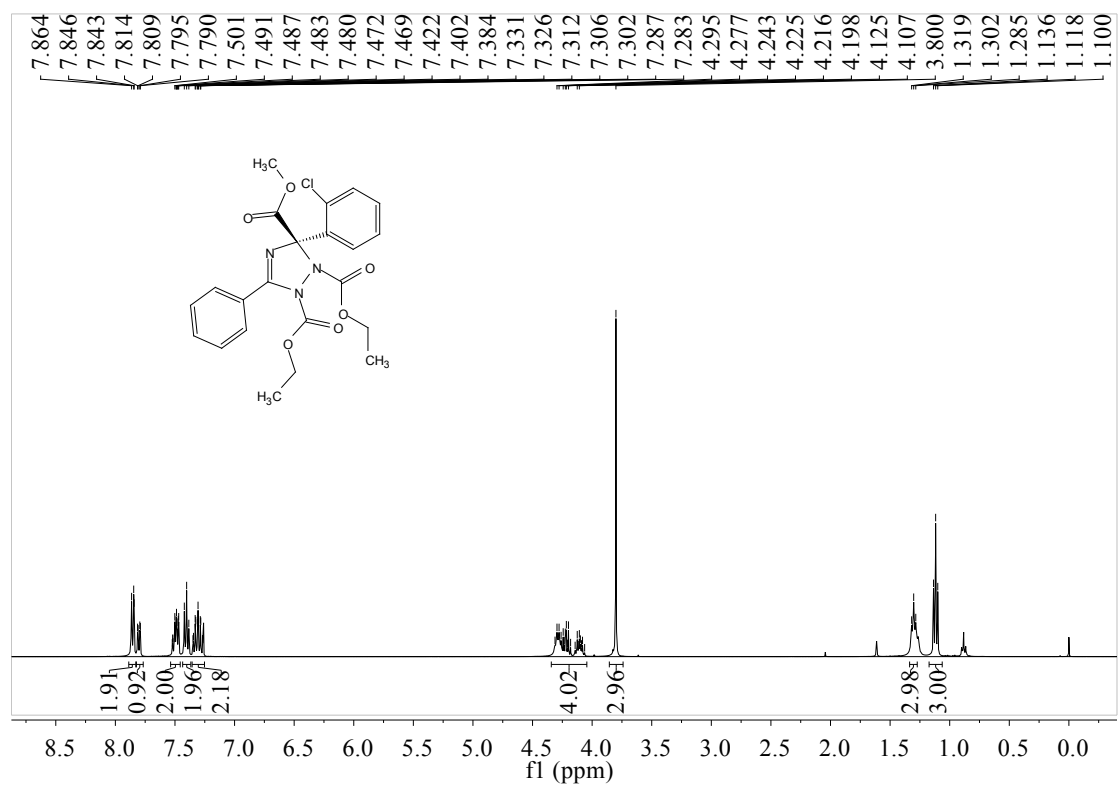
1,2-di-tert-butyl 3-methyl (R)-5-phenyl-3-(p-tolyl)-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate
(3vb)



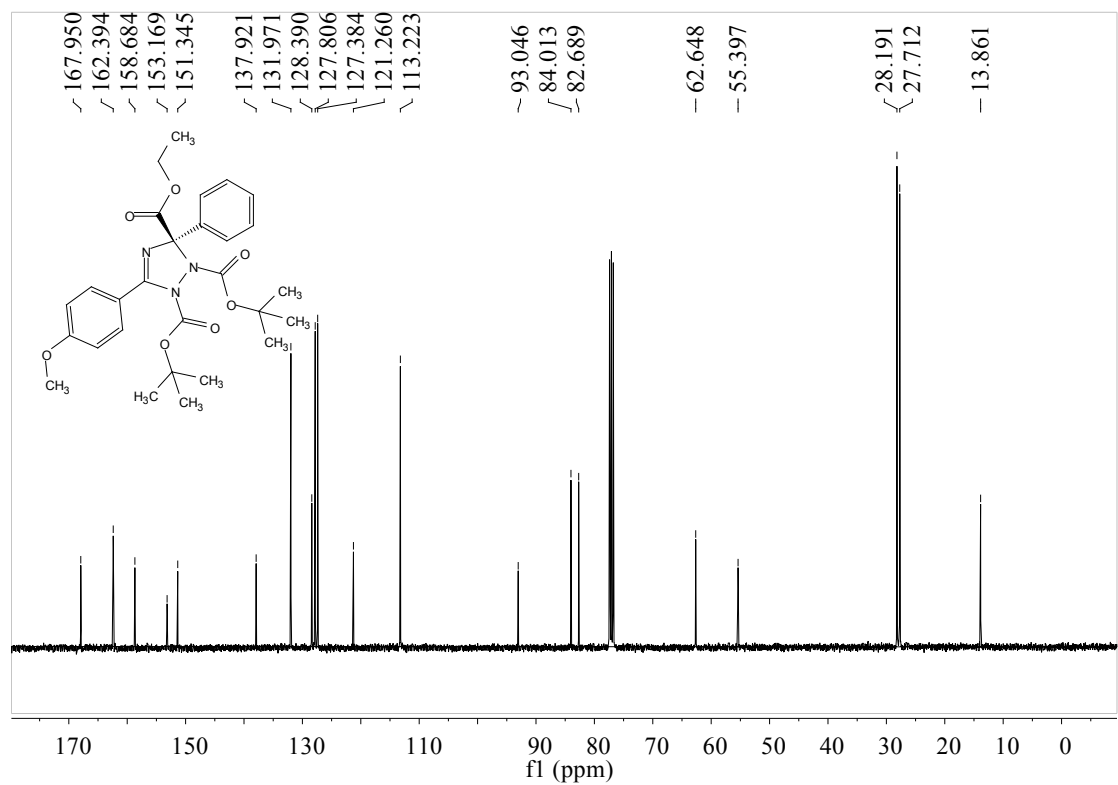
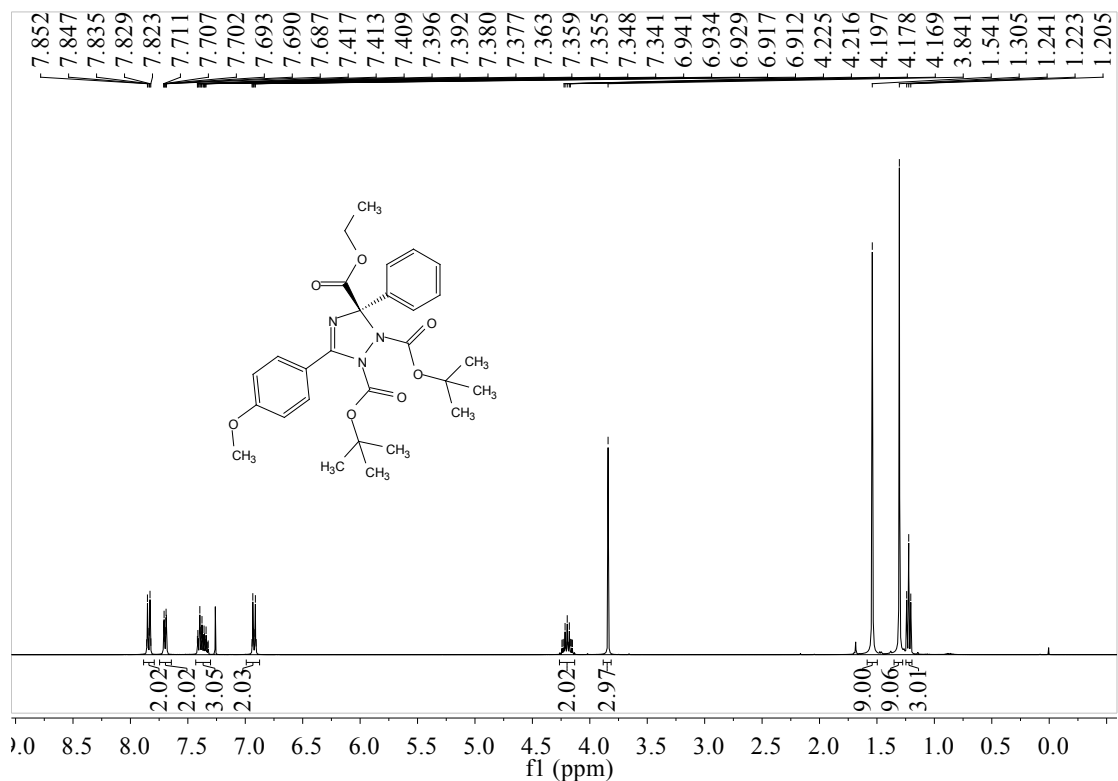
1,2-di-tert-butyl 3-methyl (R)-3-(3-chlorophenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(H)-
ntricarboxylate (**3wb**)



1,2-diethyl 3-methyl (R)-3-(2-chlorophenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(H)-tricarboxylate
(3xa)

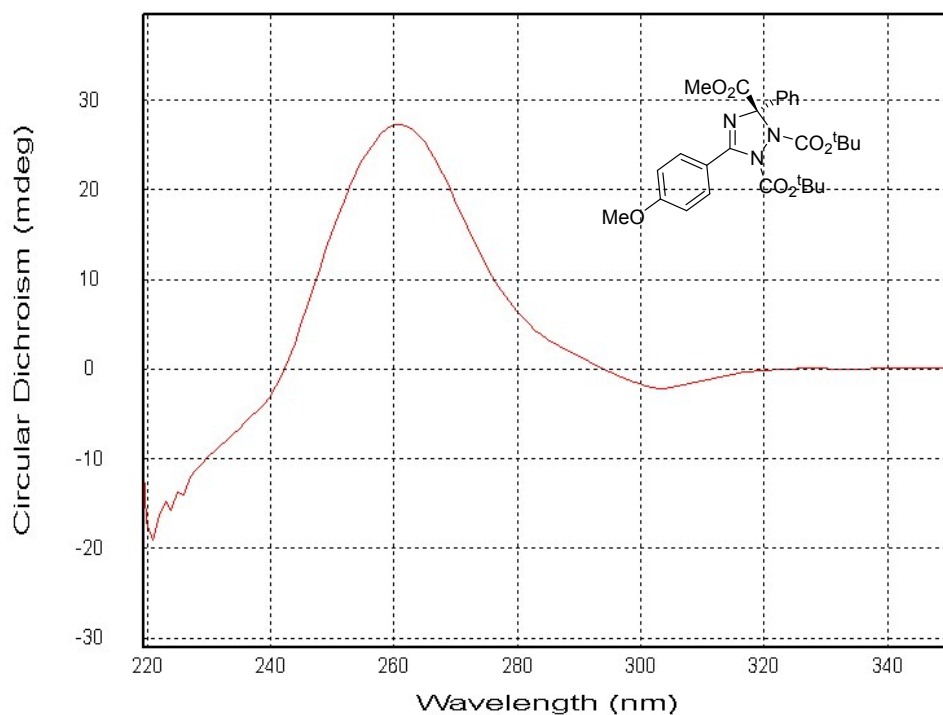


1,2-di-tert-butyl 3-ethyl (R)-5-(4-methoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(H)-tricarboxylate (**3yb**)

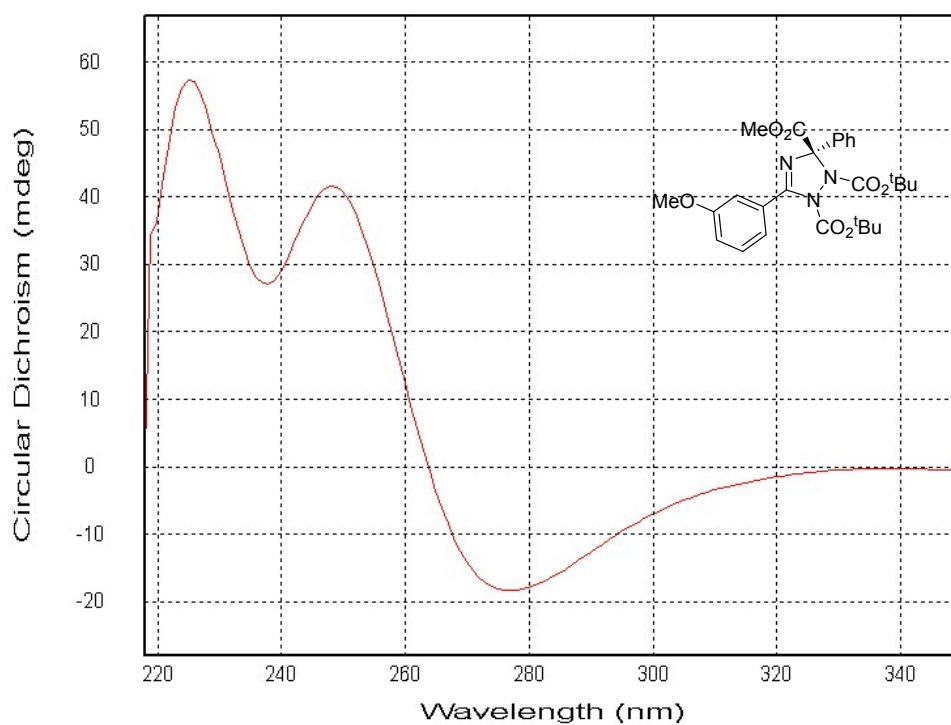


(I) CD information of the products

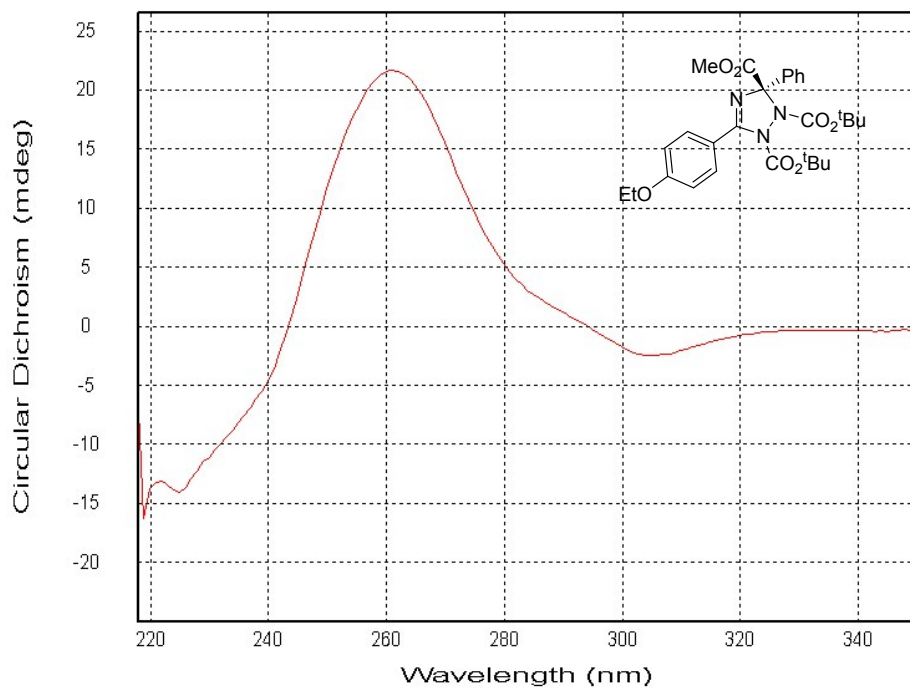
1,2-di-tert-butyl 3-methyl (R)-5-(4-methoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3ab**)



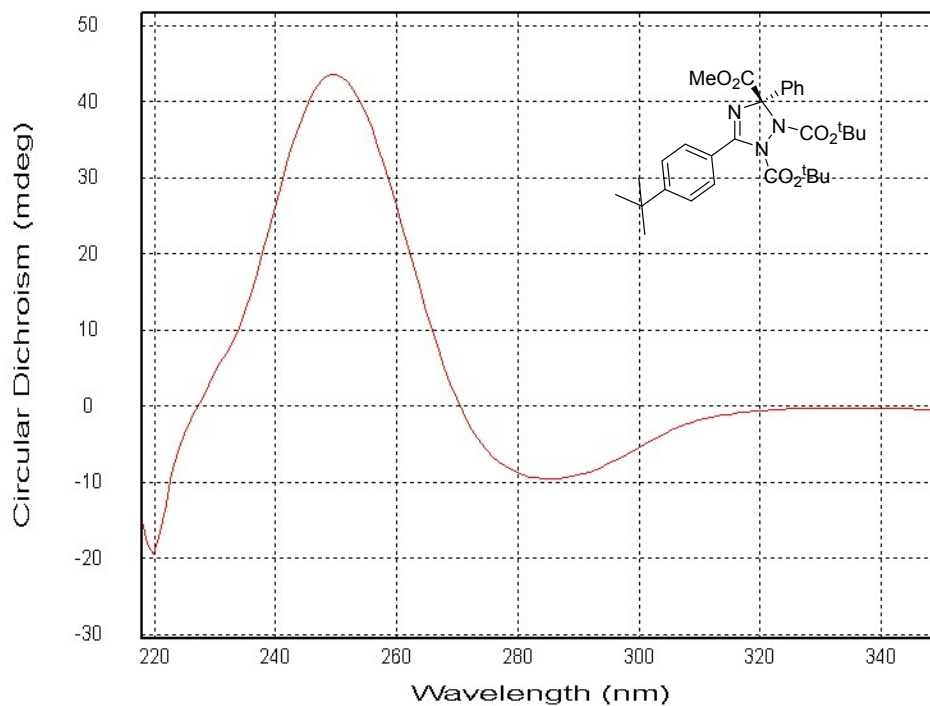
1,2-di-tert-butyl 3-methyl (R)-5-(3-methoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3bb**)



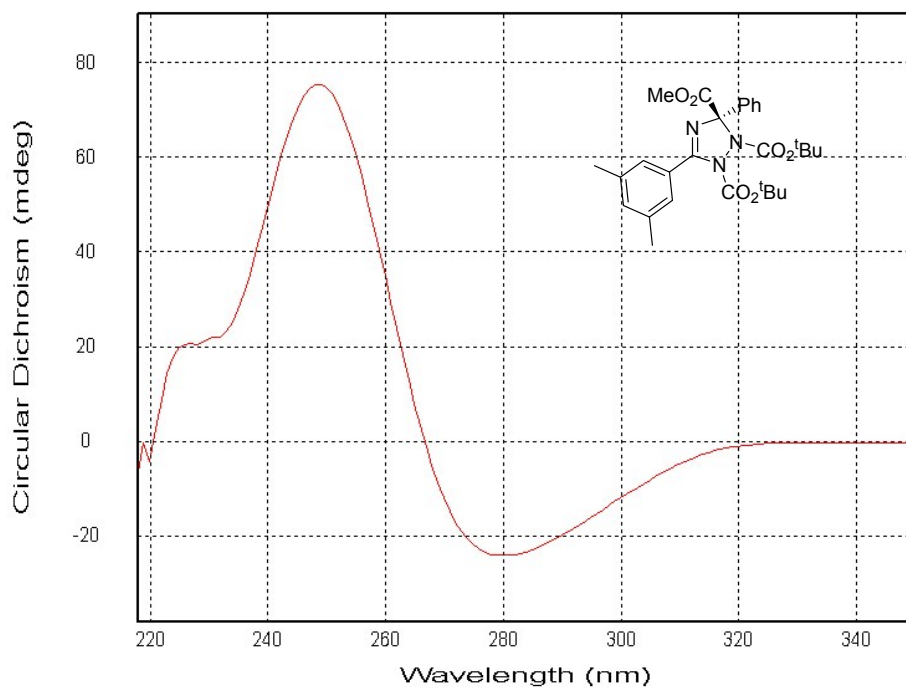
1,2-di-tert-butyl 3-methyl (R)-5-(4-ethoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3cb**)



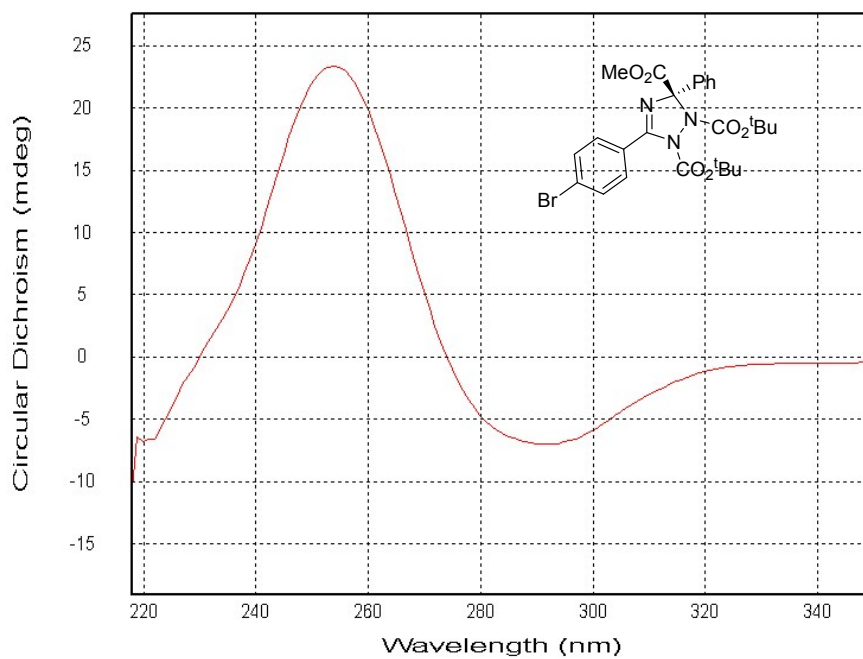
1,2-di-tert-butyl 3-methyl (R)-5-(4-(tert-butyl)phenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3db**)



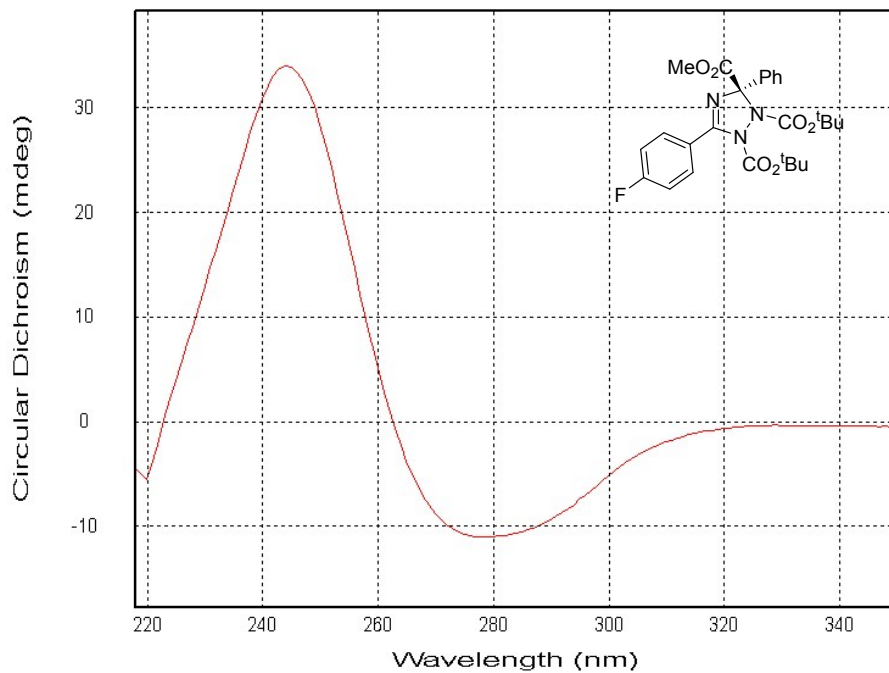
1,2-di-tert-butyl 3-methyl (R)-5-(3,5-dimethylphenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3eb**)



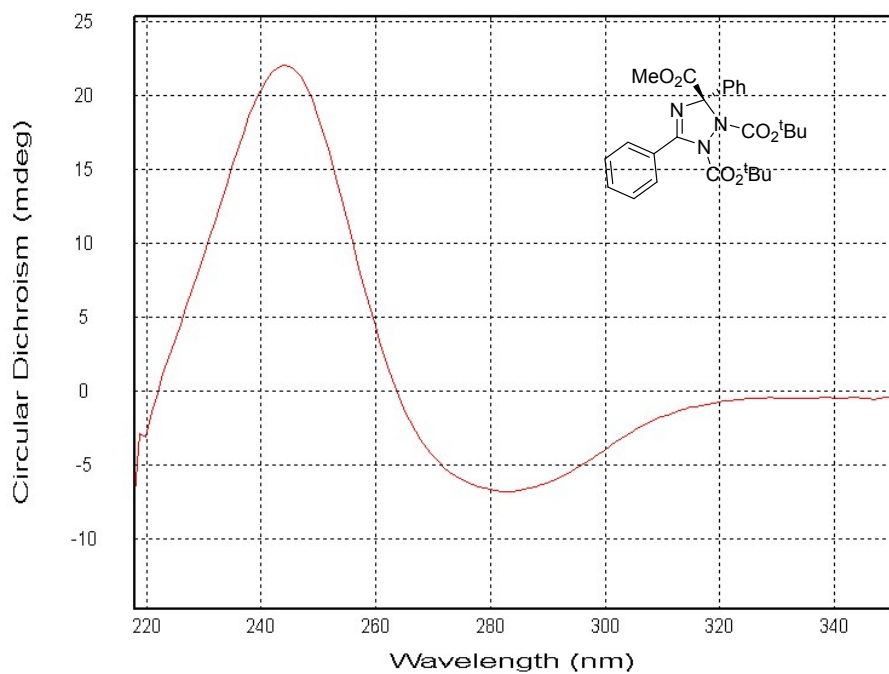
1,2-di-tert-butyl 3-methyl (R)-5-(4-bromophenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3fb**)



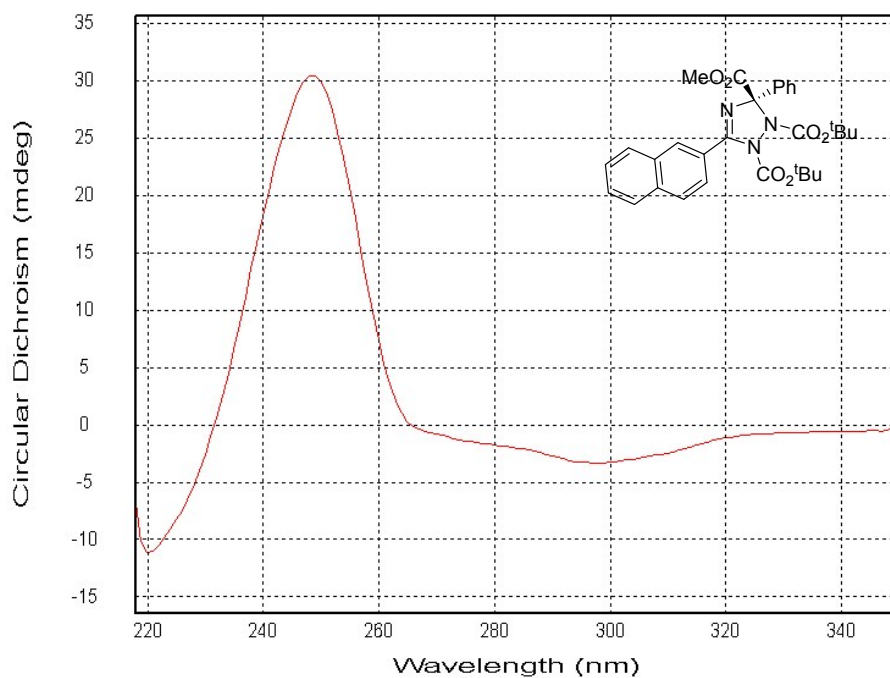
1,2-di-tert-butyl 3-methyl (R)-5-(4-fluorophenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3gb**)



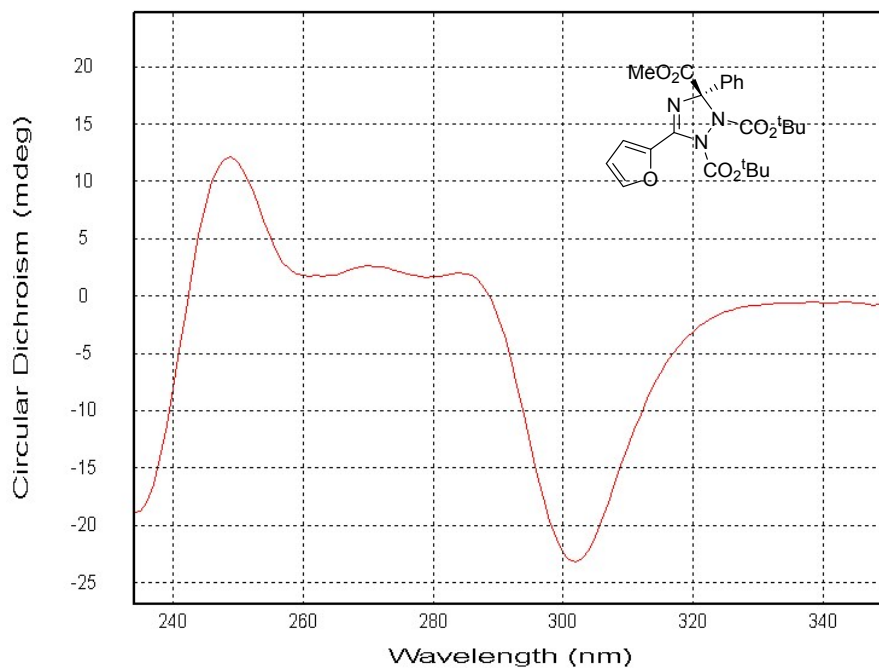
1,2-di-tert-butyl 3-methyl (R)-3,5-diphenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3hb**)



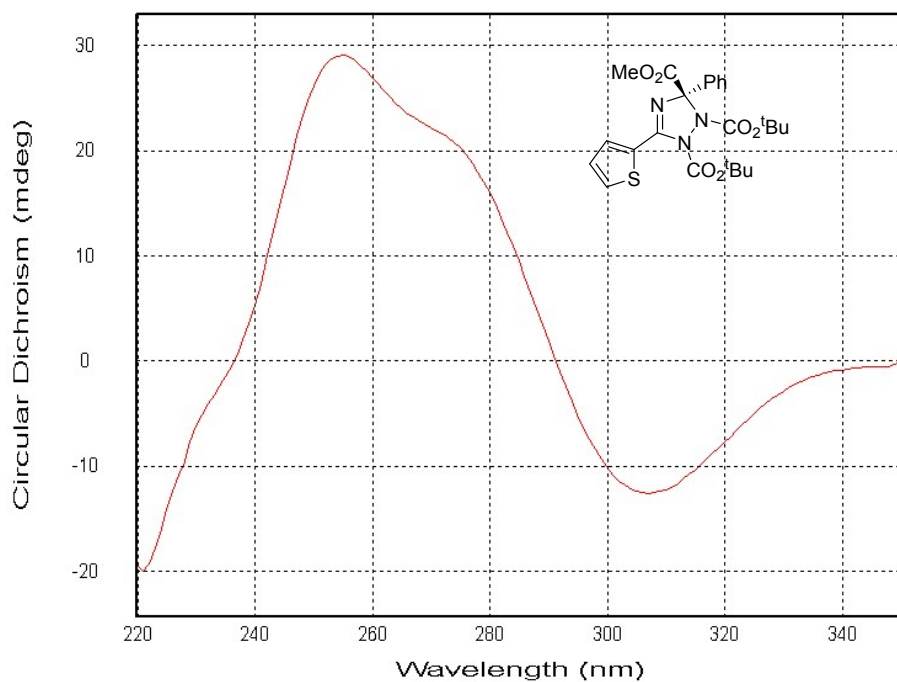
1,2-di-tert-butyl 3-methyl (R)-5-(naphthalen-2-yl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3ib**)



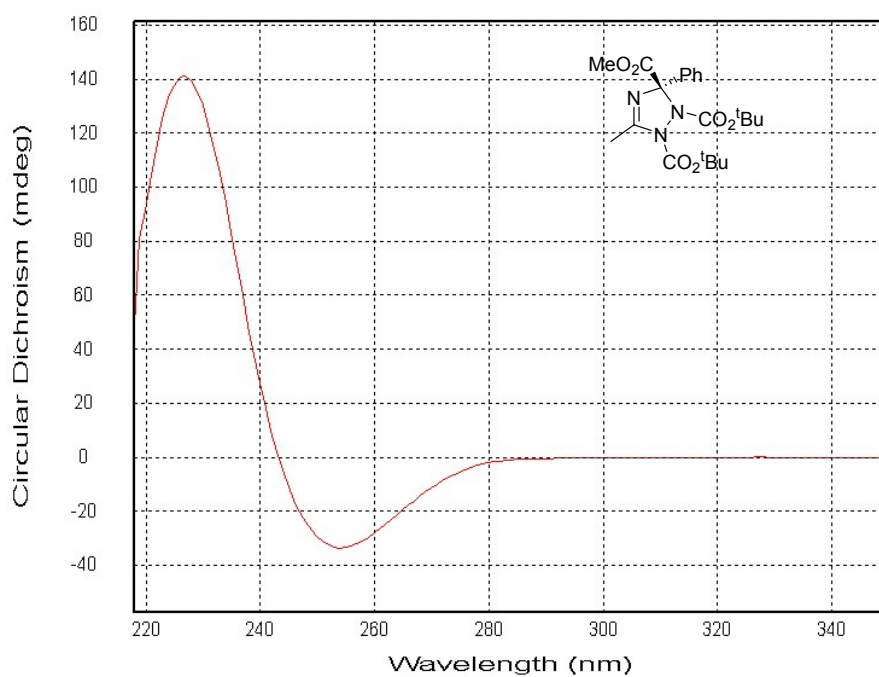
1,2-di-tert-butyl 3-methyl (R)-5-(furan-2-yl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3jb**)



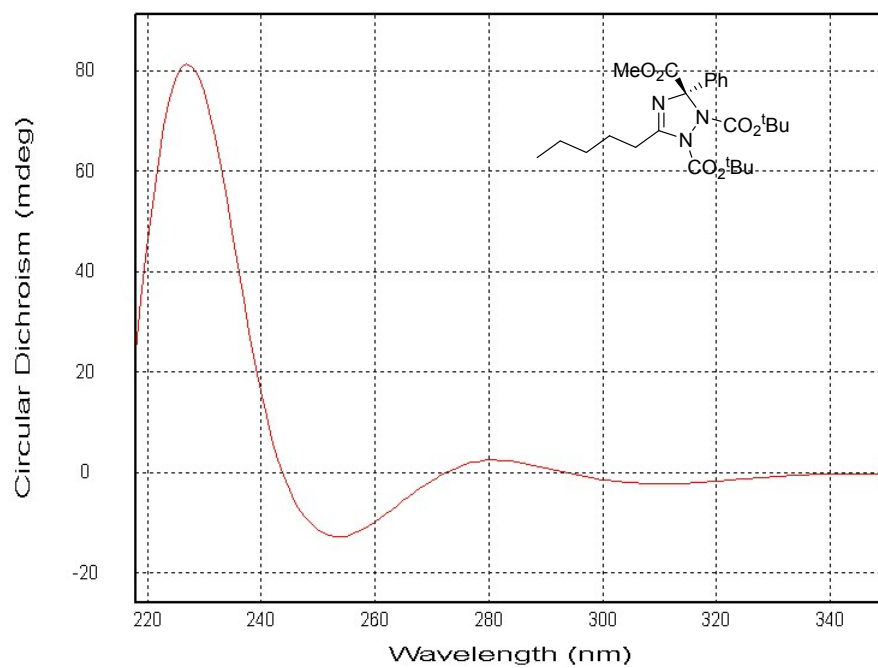
1,2-di-tert-butyl 3-methyl (R)-3-phenyl-5-(thiophen-2-yl)-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3kb**)



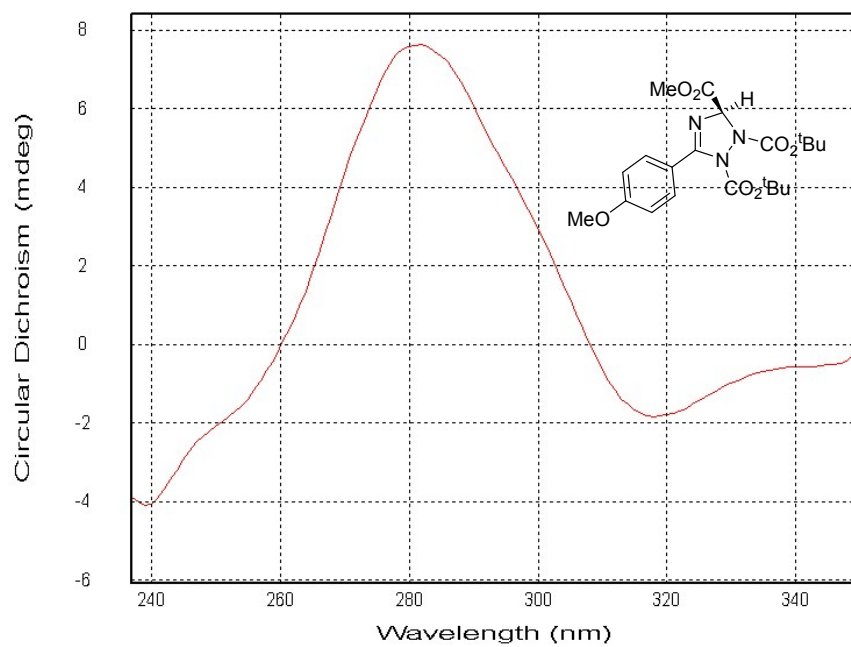
1,2-di-tert-butyl 3-methyl (R)-5-methyl-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3lb**)



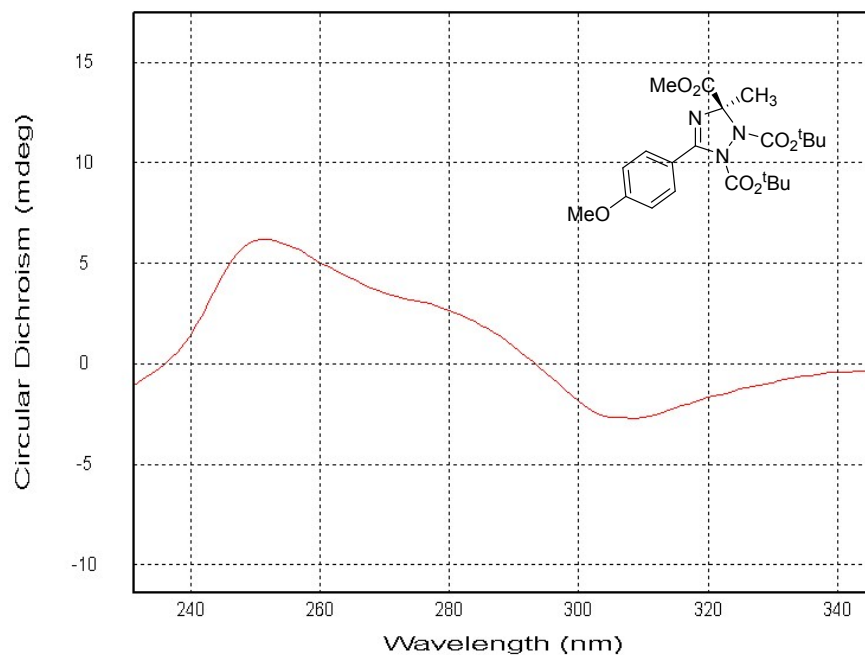
1,2-di-tert-butyl 3-methyl (R)-5-pentyl-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3mb**)



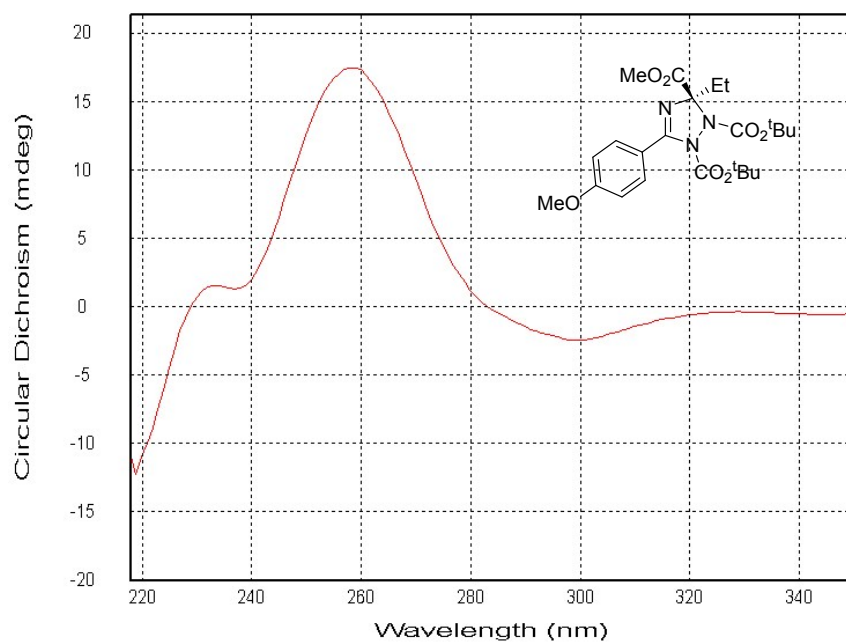
1,2-di-tert-butyl 3-methyl (R)-5-(4-methoxyphenyl)-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3nb**)



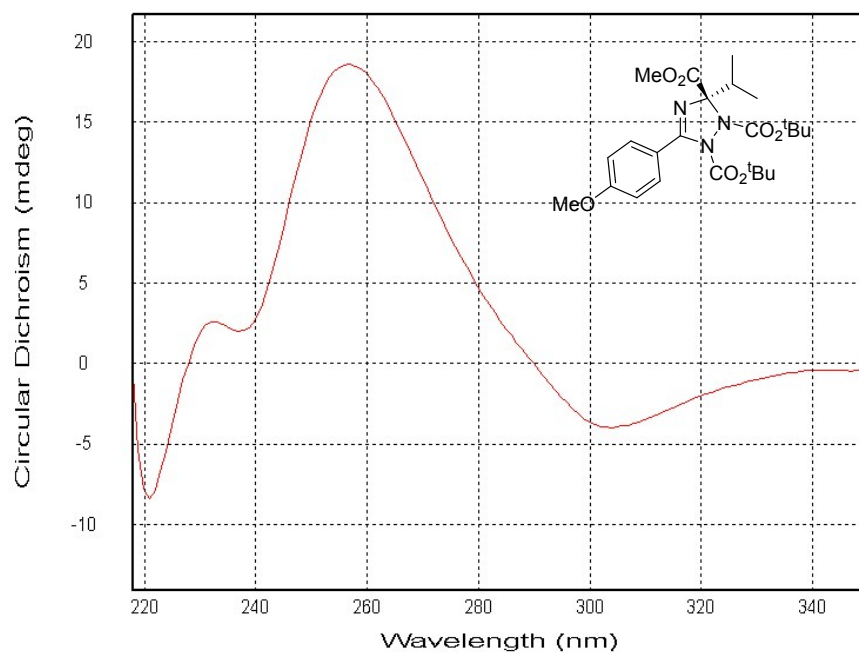
1,2-di-tert-butyl 3-methyl (R)-5-(4-methoxyphenyl)-3-methyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3ob**)



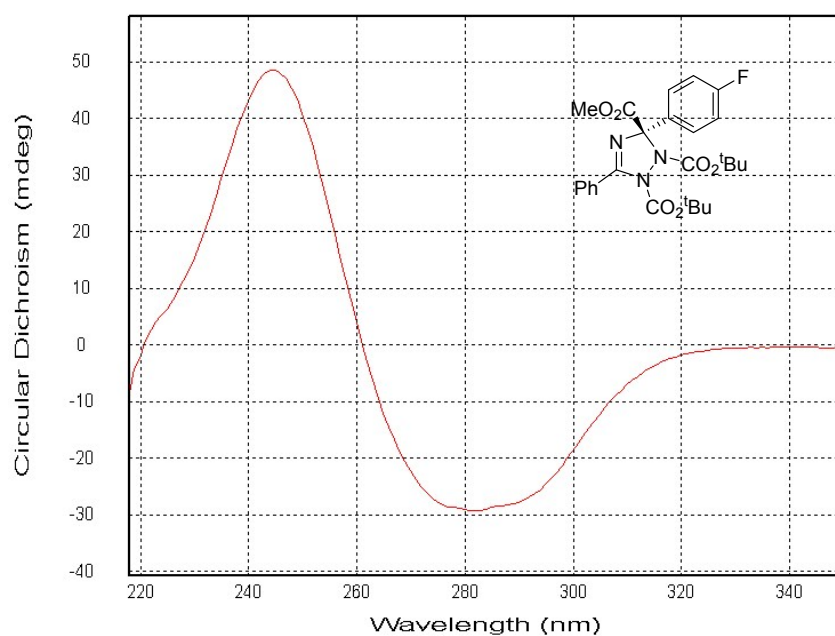
1,2-di-tert-butyl 3-methyl (R)-3-ethyl-5-(4-methoxyphenyl)-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3pb**)



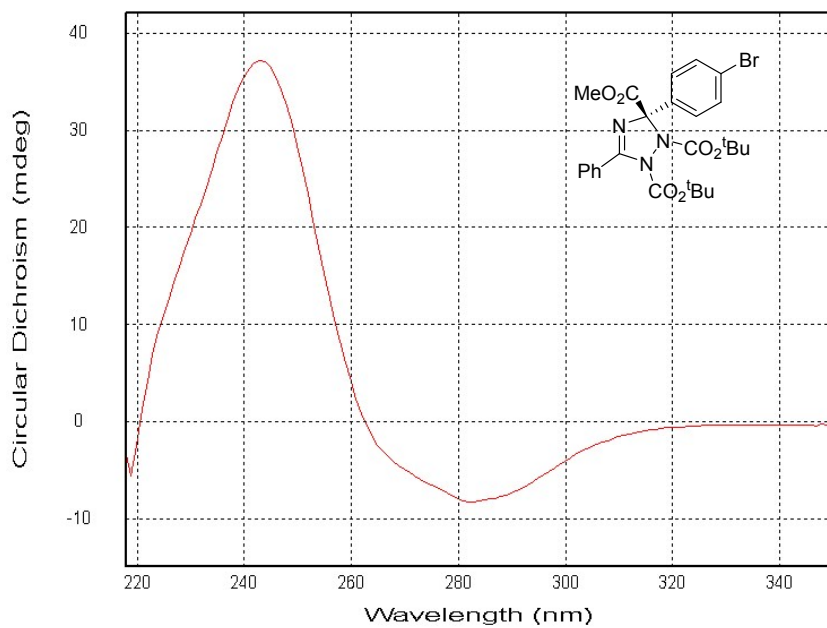
1,2-di-tert-butyl 3-methyl (R)-3-isopropyl-5-(4-methoxyphenyl)-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3qb**)



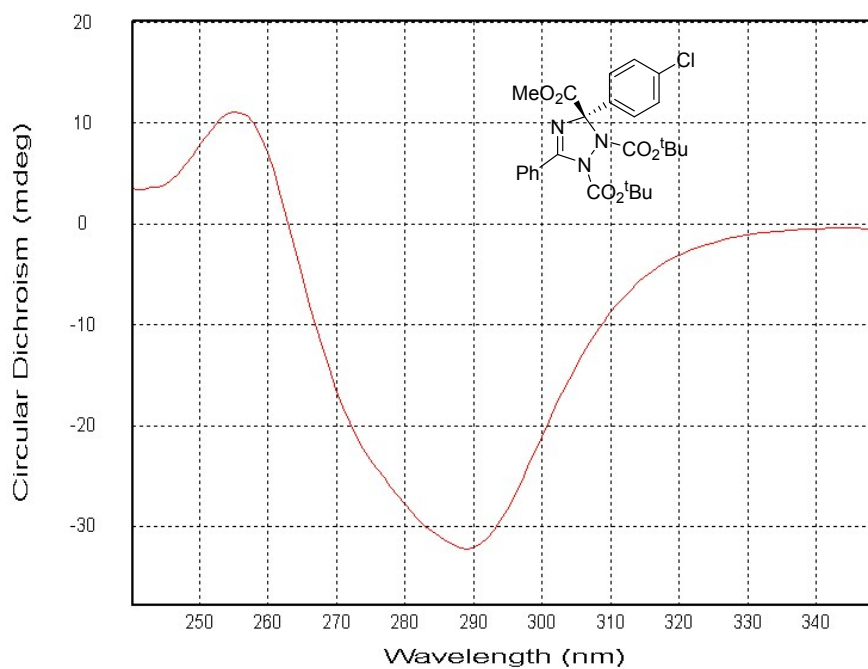
1,2-di-tert-butyl 3-methyl (R)-3-(4-fluorophenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3rb**)



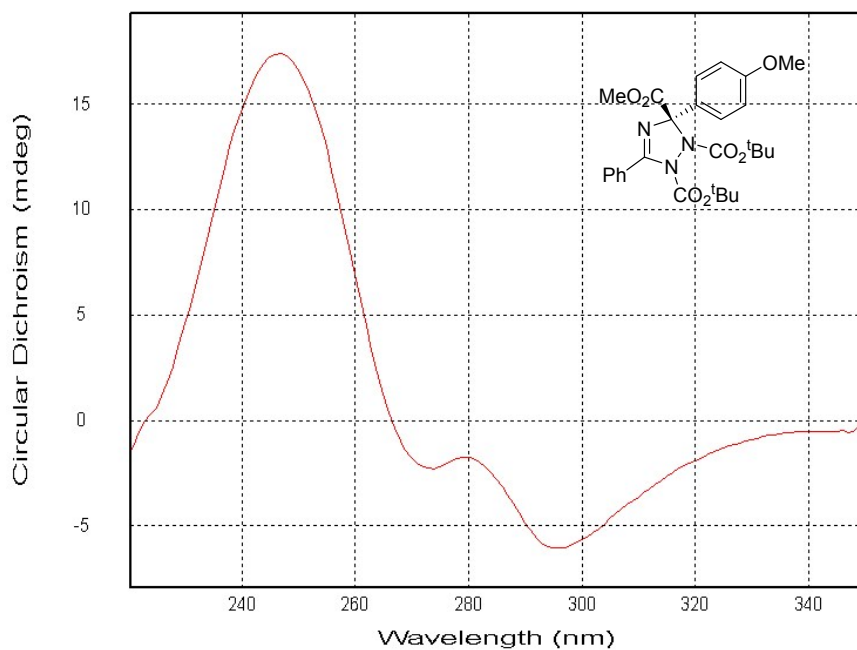
1,2-di-tert-butyl 3-methyl (R)-3-(4-bromophenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3sb**)



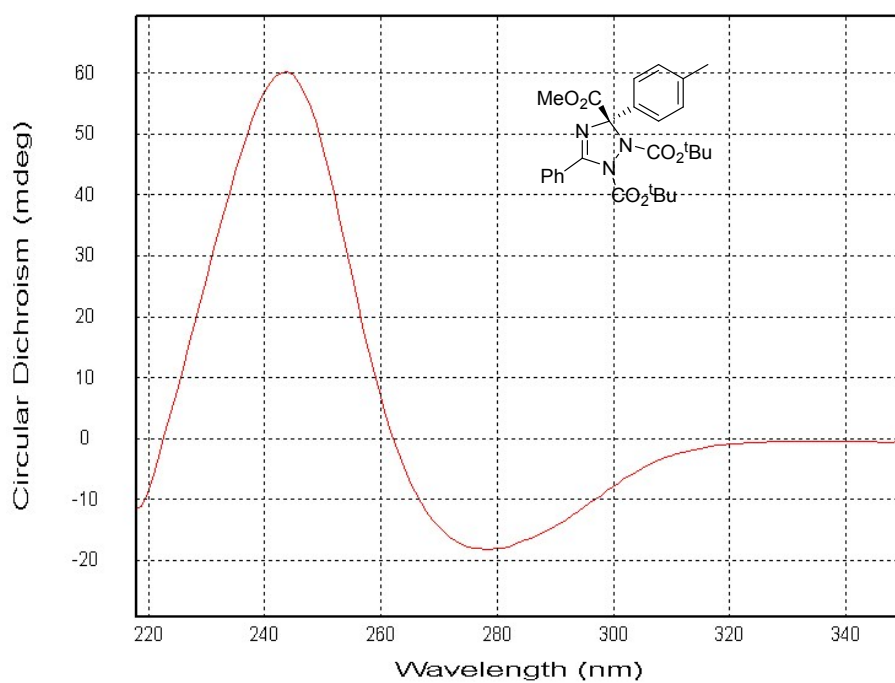
1,2-di-tert-butyl 3-methyl (R)-3-(4-chlorophenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3tb**)



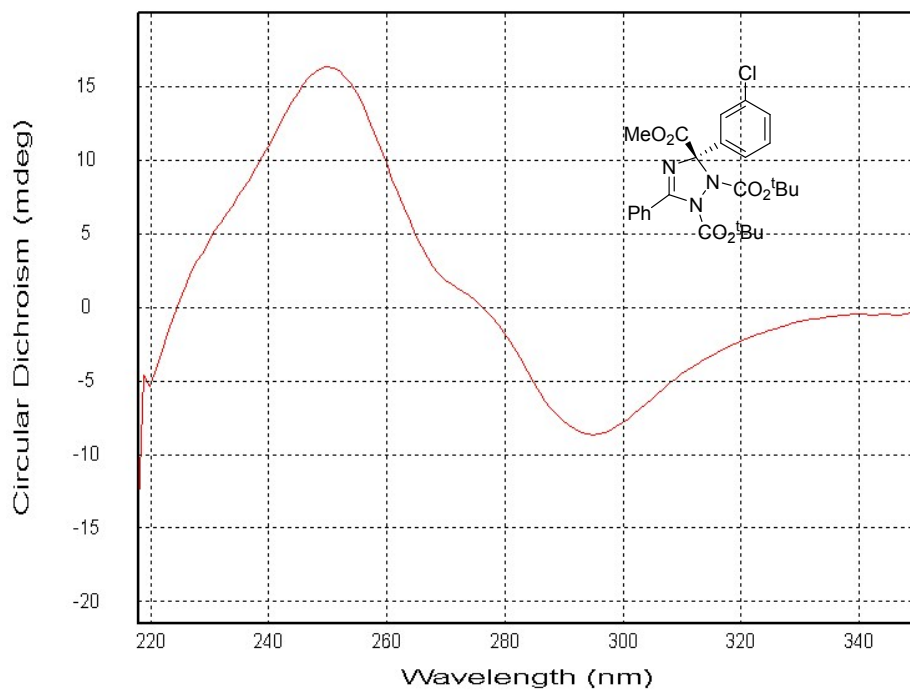
1,2-di-tert-butyl 3-methyl (R)-3-(4-methoxyphenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3ub**)



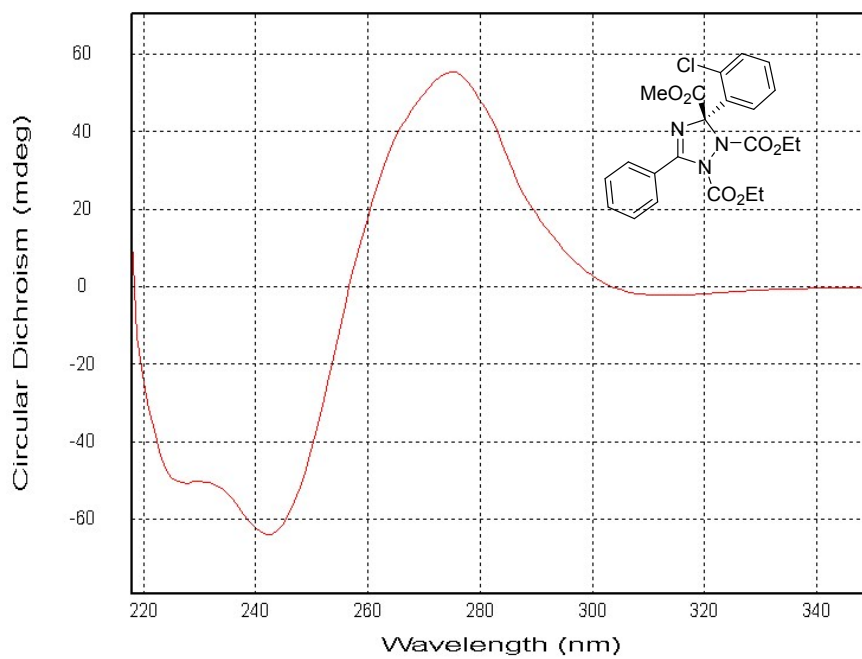
1,2-di-tert-butyl 3-methyl (R)-5-phenyl-3-(p-tolyl)-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3vb**)



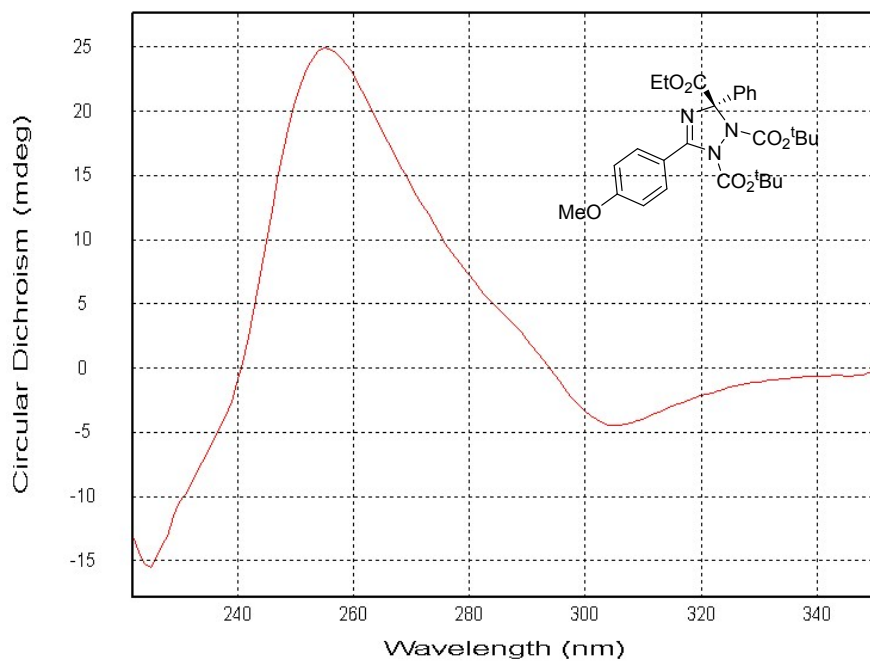
1,2-di-tert-butyl 3-methyl (R)-3-(3-chlorophenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3wb**)



1,2-diethyl 3-methyl (R)-3-(2-chlorophenyl)-5-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3xa**)



1,2-di-tert-butyl 3-ethyl (R)-5-(4-methoxyphenyl)-3-phenyl-1H-1,2,4-triazole-1,2,3(3H)-tricarboxylate (**3yb**)



(J) References

- [1] Li, P. X.; Evans, C. D.; Wu, Y. Z.; Cao, B.; Hamel, E.; Joullière, M. M.; *J. Am. Chem. Soc.* **2008**, *130*, 2351–236.