Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPLEMENTARY MATERIAL

Tris(pentafluorophenyl)borane as an Efficient Catalyst in the Guanylation Reaction of Amines. A Combined Experimental and Theoretical Investigation of the Catalytic Cycle

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Table 1S. Cartesian Coordinates of the Optimized geometries at M02-2X/6-31G* level of theory of the most stable structures for reagents, transition states and products of the studied compounds in gas phase.

REAGENTS AND PRODUCTS

Aniline

C	1.20013800	-1.18706500	0.00000000
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C	1.14835300	1.22093300	0.00000100
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C	-0.92401300	-0.03053900	-0.00000300
C	-0.19218300	-1.21660000	-0.00000400
H	1.75997700	-2.11754500	0.00000000
H	2.95874600	0.05538600	0.00000300
H	1.66710500	2.17507200	0.00000200
H	-0.81171000	2.11615400	0.00000100
H	-0.73919300	-2.15391900	-0.00000800
N	-2.36256100	-0.12073400	-0.00000400
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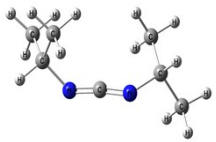
H	-2.73688600	0.36364000	-0.81328000

Carbodimide



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C	1.64393900	1.40139900	0.55649900
C	3.29974000	-0.14242500	-0.56611600
H	2.57276800	-0.32450600	1.44058200
H	0.84380200	1.47194700	1.30070700
H	2.44167800	2.09319300	0.84275600
H	1.24265300	1.72198500	-0.41178500
H	3.64986000	-1.17502900	-0.63446800
H	2.93660700	0.16488700	-1.55229600
H	4.14214700	0.49902900	-0.28935800
C	-2.29354300	-0.29779700	-0.26685200
C	-2.72321600	1.12782700	-0.60227200
C	-2.24337900	-0.53480500	1.23871200
H	-3.01383400	-0.99210600	-0.71458500
H	-2.74013600	1.27945400	-1.68410000
H	-3.71989200	1.33275200	-0.19956400
H	-2.01705500	1.84226400	-0.16505600
H	-1.92290400	-1.55577800	1.46592800
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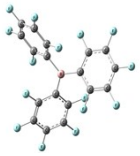
$B(C_6F_5)_3$



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C	2.09456900	1.40913500	-0.62823000
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C	-0.28139600	-3.82318600	-0.65336100
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F	3.93187100	2.74580800	-1.27084600
F	5.62483200	1.04668200	-0.00037500
F	4.65638200	-1.14803900	1.27058300
F	2.04084200	-1.65137600	1.27165200
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F	-2.43913900	-0.94073500	1.28953900
F	-3.31313800	-3.45529500	1.28450200
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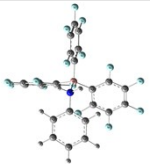
Aniline- $B(C_6F_5)_3$



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C	3.74133700	-1.47563100	1.42392100
C	4.24220500	-1.80774000	0.17600500
C	0.27497900	1.36084600	-0.26704300
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C	0.91345300	2.40790100	0.38950800
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C	1.17774600	3.64797100	-0.17095900
C	0.82295400	3.87090700	-1.49310100
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C	-0.92635800	-2.45680100	-0.22144000
C	-2.25949500	-0.56504100	-0.62150700
C	-1.93563200	-3.29244800	-0.68909600
C	-3.29241600	-1.36017000	-1.09337000
C	-3.12607500	-2.73814800	-1.13192600
F	2.03447200	-0.67306100	2.78001600
F	4.48809900	-1.64426600	2.51257100
F	5.47162100	-2.29603600	0.05410000
F	3.91615200	-1.93780600	-2.15166000
F	1.43569600	-0.94918900	-1.90443300
F	1.31095700	2.25142500	1.67950200
F	1.77149500	4.60491000	0.53958400
F	1.06938800	5.04349900	-2.06567300
F	-0.12495600	3.05067900	-3.48070700
F	-0.61791100	0.70648000	-2.37026700
F	-2.50434600	0.74986900	-0.56695700
F	0.17572500	-3.07273800	0.23273300
F	-1.77030700	-4.61356800	-0.70209800
F	-4.10643900	-3.51811900	-1.57299800
F	-4.44353600	-0.81993800	-1.48726000
N	-0.32847900	0.10113400	2.01781500
H	-0.24612700	-0.81483200	2.46507800
H	0.37589800	0.68808500	2.47024300
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C	-2.74039200	-0.21773800	2.37821500
C	-1.82175800	2.02469500	2.32784100
C	-4.01566800	0.31340500	2.54429100
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H	-0.95923000	2.67984200	2.26178800
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H	-4.86611000	-0.35498900	2.62888700
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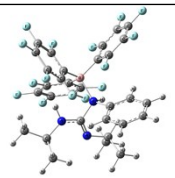
I2



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C	-3.79419900	-2.08271900	1.93129200
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C	-0.93367700	1.49077500	-0.22154600
C	-1.37023600	2.34842800	0.79119600
C	-2.06042500	3.52601500	0.56190900
C	-2.35913400	3.89207600	-0.74577100
C	-1.96347900	3.06906700	-1.78569300
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C	-0.16558800	-1.33847300	-3.25950600
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C	-0.79213600	-2.14134700	-4.20823400
H	-0.75277200	-1.85356800	-5.25376000
C	-1.45742000	-3.30362000	-3.82826300
H	-1.94410000	-3.92132800	-4.57584000
C	-1.48022700	-3.68095800	-2.48851500
H	-1.97735300	-4.59597800	-2.18374100
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H	-0.84355200	-3.19190300	-0.48728300
C	1.82379000	-0.49504200	-1.35857400
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C	2.99593200	2.92694900	-1.99019100
H	2.17918800	3.31021300	-2.61322300
H	3.92069300	3.41391900	-2.30976700
H	2.80180200	3.20323900	-0.94994000
C	3.46812100	1.01623600	-3.57869500
H	3.50199800	-0.07225100	-3.67148200
H	4.44676100	1.41868400	-3.85753300
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C	3.93778900	-3.05027900	-0.22515100
H	4.88195100	-2.68793500	-0.64225200
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F	3.41613200	-1.81989900	3.07161000
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F	-4.86639800	-2.71300300	2.39624000
F	-4.77037500	-1.90714600	-0.20590100
F	-2.63901600	-0.60258700	-1.12681500
F	-1.10782900	2.03495700	2.06776100
F	-2.43961700	4.30486100	1.57201800
F	-3.01503900	5.02039100	-0.99244600
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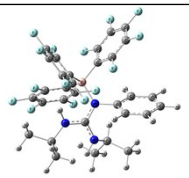

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C	1.08886300	2.53764300	-0.70160300
C	1.64606600	3.77742000	-0.43760500
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C	0.72283100	-1.74566700	2.99084900
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H	1.69324000	-2.67145900	4.66393800
C	1.88678700	-3.85671100	2.87471300
H	2.46150100	-4.64135500	3.35640200
C	1.58357300	-3.94166100	1.51938500
H	1.91673200	-4.79566700	0.93792700
C	0.84586000	-2.93771900	0.89569000
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H	-3.03249000	3.21686900	1.42032400
H	-4.73760300	2.77161100	1.57171700
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H	-4.59655400	-2.86270100	1.77786300
H	-3.98786800	-3.94677000	0.51954600
H	-4.04419900	-2.19954500	0.21953400
C	-2.11390400	-3.91163800	2.56245400
H	-1.09687800	-3.80031300	2.94610900
H	-2.21225000	-4.90147500	2.10769600
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F	-1.62217700	2.46914300	-0.94820200
F	-3.81728100	2.29581500	-2.38359000
F	-4.61120300	-0.08876700	-3.45359000
F	-3.10366700	-2.32109100	-2.99697900
F	-0.88206100	-2.17034300	-1.55471200
F	0.78278300	-0.78462800	-3.06713800
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F	4.95474700	-1.24416300	0.36386900
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F	0.91305200	2.20878500	-1.98856300
F	1.98686700	4.60275100	-1.42538900
F	2.38482500	5.34494700	1.16342900
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N	-0.34056000	-0.77216100	1.01772500
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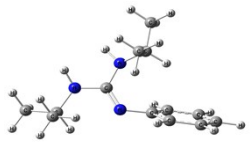
H	-3.06717700	-1.18257900	2.68661500

Guanidine



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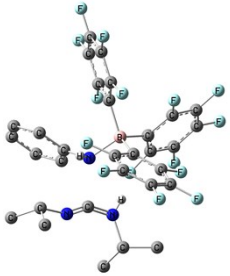
C	3.17124100	-1.55797800	0.98771100
H	3.73864800	-1.84089900	1.86983000
C	3.81627300	-1.41089800	-0.23770400
H	4.88589300	-1.57616500	-0.31928200
C	3.06929100	-1.06011900	-1.36167800
H	3.55772500	-0.95291900	-2.32628100
C	1.69932600	-0.84755700	-1.26287500
H	1.11645400	-0.56976300	-2.13632100
C	-0.93426000	0.24818800	-0.29971900
C	-3.08913300	-0.94934700	-0.16490200
H	-2.51496800	-1.78849800	-0.56672300
C	-3.25811800	-1.14603800	1.34107200
H	-2.27839700	-1.21311700	1.81910800
H	-3.81579500	-2.06380400	1.55330700
H	-3.81380800	-0.30566100	1.77579000
C	-4.43204300	-0.85061500	-0.88029100
H	-5.00608400	0.00866200	-0.51074900
H	-5.02917000	-1.74859100	-0.69743100
H	-4.29292600	-0.73263500	-1.95802400
C	0.76298000	2.04260200	0.13328600
H	1.66347000	1.44993400	-0.05611800
C	0.99564000	3.45220500	-0.39690700
H	1.19256800	3.43673000	-1.47269900
H	1.85123900	3.91050500	0.10535400
H	0.11922700	4.08571000	-0.20934800
C	0.48189500	2.04282900	1.63444300
H	-0.39717200	2.65878700	1.85943800
H	1.33766500	2.44835000	2.18312300
H	0.29616800	1.02601000	1.99303400
N	-0.33867300	-0.81872300	0.10200200
N	-2.30705000	0.24619900	-0.47492200
N	-0.34188600	1.45636800	-0.63702300
H	-0.99083200	2.13716600	-1.01355200
H	-2.76354300	1.11320600	-0.21212900

Transition States and guanidine adducts

TS1



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C	2.25591700	1.63495700	2.80502400
C	2.81304900	0.52410200	3.38414600
C	2.37977700	-0.71746600	2.97599200
C	1.39778200	-0.80600600	2.02040500
C	-1.67752500	-0.89904300	0.62382000
C	-1.94101300	-1.45488900	1.86735800
C	-3.05721000	-2.21721000	2.14753400
C	-3.99795400	-2.43944200	1.17187500
C	-3.80994800	-1.88120200	-0.07065200
C	-2.68184700	-1.12895500	-0.31008900
C	-1.04181700	1.50723300	-0.27097500
C	-1.89432000	2.12839100	0.64042200
C	-2.58289100	3.29041600	0.39115200
C	-2.43501900	3.92503600	-0.82415200
C	-1.58499800	3.37915000	-1.74937300
C	-0.91963200	2.20615900	-1.45011200
C	0.03700900	-1.58339400	-1.99922000
C	-0.03986500	-1.08930100	-3.29551500
H	0.21150000	-0.07075000	-3.50148500
C	-0.45578300	-1.90550300	-4.33424500
H	-0.51535700	-1.49857300	-5.32801100
C	-0.78902300	-3.23051500	-4.10872900
H	-1.11157800	-3.85767700	-4.91984000
C	-0.69968200	-3.73467100	-2.82305700
H	-0.95298700	-4.76074600	-2.62410100
C	-0.28828200	-2.92011600	-1.78119400
H	-0.23381700	-3.32337000	-0.78465000
C	2.57992600	-0.35552100	-1.30873700
C	3.69629300	1.74744100	-1.78830500
H	4.46271600	1.40164800	-1.10596200
C	3.35163900	3.19649100	-1.46247600
H	2.57231100	3.56530200	-2.12257700
H	4.22595500	3.82235600	-1.59823400
H	3.00980900	3.29733800	-0.43982900
C	4.17572100	1.56710000	-3.22602400
H	4.40347000	0.52818400	-3.43718100
H	5.07574000	2.14899500	-3.39439300
H	3.41859800	1.90125300	-3.92775500
C	3.50159500	-2.70456300	-0.91080400
H	2.60541600	-3.09141600	-0.44380000
C	4.65734200	-2.78396100	0.08131900
H	5.55696100	-2.35054300	-0.34113000
H	4.85563200	-3.82280100	0.31927000
H	4.41873400	-2.26793000	1.00289900
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H	4.65912700	-3.08270800	-2.69519300
F	0.86411500	2.64517700	1.31505700
F	2.67725100	2.83780800	3.14995300
F	3.75985600	0.63791300	4.29088600
F	2.92699200	-1.80883000	3.48208100
F	1.06826000	-2.05222000	1.65826800
F	-1.12877600	-1.25973100	2.89730700
F	-3.23139200	-2.72394600	3.35515600
F	-5.06745300	-3.16486800	1.42492400
F	-4.71152400	-2.06226100	-1.01880100
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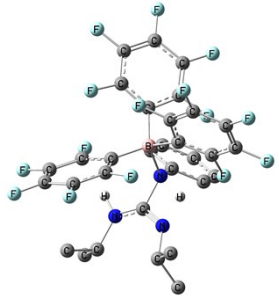
TS2



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C	-3.36520700	-1.17666000	-2.59701200
C	-2.65246800	-2.12368500	-1.87352100
C	-1.52830500	-1.72821300	-1.17104300
C	1.58912200	-1.00792300	-0.44562000
C	1.76652800	-1.93595900	-1.46942300
C	2.95377900	-2.63478600	-1.67052000
C	4.04154200	-2.39776400	-0.84658300
C	3.93089800	-1.45317600	0.16386900
C	2.73220600	-0.77523500	0.32414900
C	0.82207700	1.44474000	-0.40901000
C	1.18762300	1.78120300	-1.71442000
C	1.78302800	2.98030500	-2.07076500
C	2.06591700	3.91913100	-1.08577400
C	1.74362400	3.63074600	0.22891200
C	1.15335400	2.40756400	0.52714500
C	0.43430100	-0.80994400	2.47770500
C	0.53901700	0.00153400	3.60377200
H	0.05433600	0.97021600	3.63183700
C	1.27509400	-0.43692400	4.70126400
H	1.35758400	0.20212900	5.57463500
C	1.90749200	-1.67578900	4.68000300
H	2.48947600	-2.00612800	5.53405500
C	1.77394400	-2.49641800	3.56282200
H	2.24158300	-3.47562300	3.54417300
C	1.02406500	-2.07513800	2.47086600
H	0.89022500	-2.71555300	1.60399000
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H	-3.80775800	1.51235700	1.19533400
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H	-2.13708800	4.07583000	1.22539200
H	-3.82287000	3.96613500	0.70094700
H	-2.55426900	3.11274500	-0.21013000
C	-3.56503100	2.55800000	3.07490500
H	-4.53474700	3.06128200	3.02283400
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H	-3.66194400	1.67716900	3.71605700
C	-3.82689700	-1.03700500	2.00854700
H	-4.16552600	-0.13266800	2.52835900
C	-3.94486700	-2.22239000	2.96332100
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H	-4.98832300	-2.37435700	3.25325900
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F	-0.91647400	-2.68478200	-0.44554200
F	0.79523100	-2.20666400	-2.34867700
F	3.05397900	-3.52024300	-2.66075800
F	5.18049300	-3.05928700	-1.02726000
F	4.97219400	-1.19691000	0.95432100
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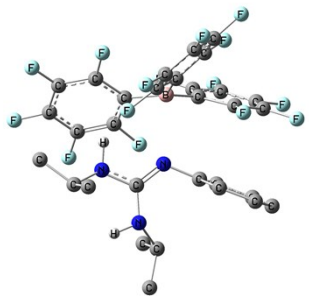
TS3



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C	-2.39545100	-1.68589500	-2.29248600
C	-1.18982800	-1.21199600	-1.80416200
C	1.76815700	-0.10644200	-1.15665300
C	2.01969500	-0.85813300	-2.30875200
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C	4.22374800	-1.45767900	-1.58427400
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C	2.83369800	-0.03560400	-0.25446500
C	0.44321700	2.06081100	-0.19952600
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C	1.62036900	4.16397900	0.27189800
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H	0.33982600	0.16186100	3.46928900
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H	2.37699700	-0.46028600	4.75209300
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H	3.94455000	-2.16105700	3.84539400
C	2.77629100	-2.49738800	2.06829100
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C	1.63393800	-2.14961100	1.35103600
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C	-3.98657800	-0.44907500	1.46597700
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C	-4.92214400	0.07486900	0.38022000
H	-5.91807300	0.25388900	0.79334900
H	-5.01043200	-0.63523300	-0.44670500
H	-4.54797100	1.02715100	-0.01643900
C	-3.92699200	0.51255400	2.65686900
H	-3.23675100	0.15219700	3.42563500
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H	-3.57919300	1.49510300	2.32345400
C	-1.15174800	-3.22607500	2.85177400
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H	-2.21294600	-4.38863500	1.36253100
C	-1.84375900	-3.90067100	4.03013400
H	-1.81593700	-3.26085800	4.91618700
H	-1.34836300	-4.84572000	4.26649700
H	-2.89129700	-4.12542100	3.79180200
F	-1.74573000	2.34458600	-1.99703500
F	-4.08565900	1.45270600	-2.89260800
F	-4.56430700	-1.21275600	-3.07558000
F	-2.63366200	-2.99160400	-2.37101900
F	-0.30901100	-2.13963900	-1.42058400
F	1.10991500	-0.94846600	-3.28300000
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F	5.36466700	-2.10593300	-1.77781100
F	4.98865600	-0.64705800	0.48835800
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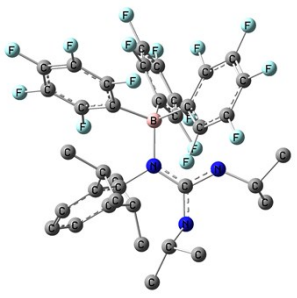
3g



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C	-3.09146100	0.41502500	-1.94382200
C	-4.31131600	0.96858200	-2.31320400
C	-5.00654600	1.76600000	-1.42092200
C	-4.45317500	2.00112500	-0.17158200
C	-3.24191800	1.40876700	0.15831100
C	-1.87670400	-1.00613200	1.31274800
C	-3.22497400	-1.41641700	1.28398800
C	-3.94274900	-1.87690900	2.37477900
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C	-1.98900300	-1.67070100	3.69913500
C	-1.31339400	-1.21610000	2.56769100
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C	-0.21614300	2.67644900	1.61240800
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H	-0.62385000	4.41202200	2.79945600
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H	-1.14458700	5.87038700	0.86573500
C	-0.82306600	4.29567300	-0.56236000
H	-1.06065500	4.92943700	-1.41113900
C	-0.51877300	2.95061300	-0.80198300
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F	-2.08302500	-3.23449300	-0.21819900
F	-1.66087400	-4.89986900	-2.14837500
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F	0.93650900	-1.73120500	-4.43616700
F	0.71063500	-0.05805800	-2.42031700
F	-2.49237400	-0.28688000	-2.92075900
F	-4.78649300	0.77427400	-3.54325800
F	-6.16845600	2.31409100	-1.76134600
F	-5.09847300	2.76078700	0.71199300
F	-2.82631000	1.62932400	1.41498200
F	-3.91604200	-1.43575400	0.13557600
F	-5.21895100	-2.22994700	2.23909300
F	-3.99896700	-2.43241700	4.67021100
F	-1.33234300	-1.78147400	4.85560500
F	0.00034800	-1.00525500	2.81188700
N	1.45672700	-1.07534700	0.71042100
H	0.58743700	-1.57378300	0.85475100
N	0.05606500	0.69105800	0.15585900
N	2.43626700	1.01638600	0.35860600
H	3.20599600	0.49748500	0.77418600
C	2.93869100	1.77887900	-0.78928600
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C	3.60216500	3.85708700	-1.80553100
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C	4.06812200	3.17782300	-2.91995300
H	3.67718500	4.93852700	-1.77195600
H	4.43567100	1.25958900	-3.79419200
H	4.48828300	3.72502500	-3.75852100
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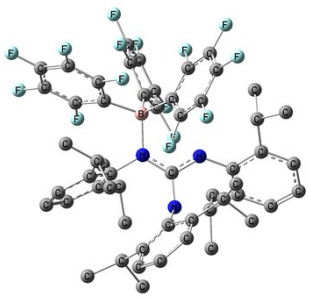

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C	1.53284100	1.14522900	-2.16137600
C	2.61710000	1.10825400	-3.02935300
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C	3.34536700	-0.90674400	-1.97780900
C	2.25578200	-0.81901200	-1.12230400
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C	2.51148100	0.81336900	1.44310300
C	3.44055500	0.67556800	2.46305400
C	3.08980900	0.03187100	3.64046900
C	1.79482500	-0.42596600	3.76592700
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C	-0.39536000	-3.22931700	0.02659500
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C	-0.36514000	-3.29552400	-2.76099000
H	-0.36437300	-3.32816100	-3.84658700
C	-0.60825900	-2.07238400	-2.12686200
C	-2.03728100	-0.73452000	0.66462400
F	1.09735300	3.06438500	1.18487100
F	-0.08631300	5.36728800	0.89624800
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F	-2.42092600	1.00971300	-1.29145000
F	0.66612100	2.14624600	-2.38954000
F	2.74499100	2.03100300	-3.98266200
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F	4.21725800	-1.90772200	-1.86845800
F	2.17898500	-1.77729200	-0.18526600
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F	4.66966200	1.16750500	2.32183800
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F	1.39757800	-1.03953400	4.88220300
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N	-2.25357900	0.24556700	1.55320100
H	-1.43589200	0.73841300	1.88419300
N	-0.87112400	-0.80430000	0.01035300
N	-3.03325600	-1.65733500	0.51982900
H	-3.71003800	-1.62924800	1.27252100
C	-0.43194200	-3.29239700	1.54383600
C	-0.80342200	-2.34467800	1.91654100
C	-1.39437400	-4.37146700	2.05484100
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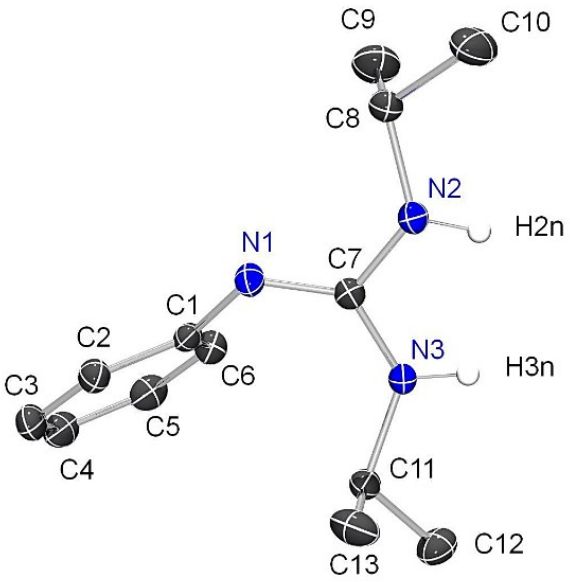
H	-2.40396400	-4.22166500	1.66010900
C	0.96664400	-3.50243500	2.13872300
H	1.67089300	-2.75143900	1.77590900
H	0.92198500	-3.43656900	3.23212600
H	1.35888500	-4.49060500	1.87188700
C	-0.85792600	-0.87319700	-3.04175700
H	-0.79166900	0.04040800	-2.45410300
C	0.20140100	-0.80868100	-4.15599200

F	-3.37404800	3.81207800	1.30814800	F	2.09236900	3.23910900	-3.33912100	F	2.69912500	4.92459900	0.11012900	C	4.58824800	-2.18722800	2.45248800	H	0.25196800	0.20574200	-4.56595500
F	-3.08257100	5.04210900	-1.07979600	F	2.63448000	5.07797700	-1.40360900	F	0.61652700	5.81173200	1.62077100	C	4.89843900	-3.32648300	1.73190000	H	1.19281900	-1.08897000	-3.79273000
F	-1.39523100	3.97094200	-2.91520800	F	2.00853900	4.50912800	1.19613800	F	-1.60659900	4.25259800	1.89344300	H	4.24020700	-4.68707900	0.21581300	H	-0.05434600	-1.48261000	-4.98109000
F	-0.07479900	1.79014400	-2.40852300	F	0.89002000	2.20100100	1.84238600	F	-1.75238300	1.91204300	0.69633800	H	5.22938700	-1.88726100	3.27529600	C	-2.24447100	-0.88567500	-3.70932700
N	2.49573700	0.93105700	-1.51303500	N	-1.81237100	1.45563400	1.72863100	N	-2.67210800	-0.66620600	0.85191100	H	5.79186500	-3.89668900	1.96597700	H	-2.46085600	-1.86803600	-4.14607900
H	1.59086500	1.30014900	-1.69881700	H	-0.96330600	2.00930600	1.74383300	H	-2.41532700	0.09306200	0.23538800	C	1.87576700	-3.63906800	-0.54825300	H	-3.05083500	-0.62059000	-3.02282600
N	3.24126500	-1.30948000	-1.23093400	N	-0.34789100	-0.44571200	1.30712900	N	-0.37927100	-0.79178500	1.10923700	H	1.38473800	-2.82402700	-1.08378500	H	-2.26122000	-0.14824000	-4.51864600
N	0.54005900	-0.79749700	-0.89946300	N	-2.42118100	-0.88997400	1.65029300	N	-1.83522400	-1.93490100	2.62535500	C	2.48613400	-4.57586300	-1.59356800	C	-3.48887200	0.55227500	2.26941600
H	0.86153600	-1.49873700	-0.26646200	H	-1.25455300	-1.41671600	1.28121400	H	-2.83303200	-2.05230400	2.75856900	H	3.34654200	-4.11952200	-2.09377100	H	-4.32433100	0.32820500	1.59564400
												H	2.81162800	-5.52300300	-1.15047500	C	-3.63830200	-2.08706900	-0.75374500
												H	1.73787200	-4.81797200	-2.35534400	H	-2.90305700	-1.899000200	-1.52820900
												C	3.10924500	-0.30629200	3.14420100	C	-3.49589500	2.04893300	2.56886600
												H	2.30663100	0.30300700	2.72905100	H	-4.41389800	2.32609100	3.09291700
												C	4.31504200	0.60661400	3.40184800	H	-2.64900700	2.31237600	3.21328500
												H	5.07190600	0.10366700	4.01207400	H	-3.42515700	2.63275600	1.64712300
												H	4.80153700	0.91927200	2.47084900	C	-3.59576300	-0.27558200	3.55331000
												H	4.00406700	1.50416400	3.94408000	H	-2.75666200	-0.03738000	4.21410200
												C	0.82704900	-4.39707900	0.28722000	H	-4.52928300	-0.05582800	4.07930400
												H	0.24555800	-3.73192900	0.93825400	H	-3.55472800	-1.35264300	3.35559700
												H	0.11801200	-4.93083900	-0.35289100	C	-4.88499300	-1.25193800	-1.03602200
												H	1.32886700	-5.13122500	0.92685600	H	-5.32527300	-1.53590000	-1.99686900
												C	2.74776100	3.96151400	0.54789100	H	-5.64542900	-1.41295200	-0.26106400
												H	1.90125700	3.48798400	1.04107000	H	-4.63691000	-0.18636600	-1.07134100
												C	3.96407300	3.87729300	1.48078000	C	-3.92565600	-3.58152000	-0.71491800
												H	4.83806600	4.33909800	1.00754000	H	-4.58566700	-3.83181000	0.12490700
												H	3.76632400	4.39988900	2.42347500	H	-4.42319000	-3.89139800	-1.63848800
												H	4.21601900	2.83850500	1.71229500	H	-2.99381700	-4.14424000	-0.61297300
												C	2.39171300	5.43001900	0.30524900				
												H	1.65201000	5.53847300	-0.49244200				
												H	1.96488300	5.85424100	1.21975800				
												H	3.27668300	6.02359400	0.04892100				
												C	3.63110500	-0.44453300	-1.88339500				
												H	2.79233700	-0.88792800	-1.34110700				
												C	4.93762700	-0.82270200	-1.16754400				
												H	4.96324500	-0.48901000	-0.12341900				
												H	5.07554200	-1.90858800	-1.16815400				
												H	5.78712400	-0.36303800	-1.68457400				
												C	3.62634600	-1.04490700	-3.29145100				
												H	3.45300200	-2.12453700	-3.23636200				
												H	2.84151200	-0.60753800	-3.90953300				
												H	4.58906500	-0.89694400	-3.79270900				
												C	0.15849800	1.91068500	2.86750800				
												H	0.46944400	0.91648700	2.57197100				
												C	1.34297400	2.56837300	3.58736400				
												H	1.11277800	3.59744300	3.88393800				
												H	1.58630400	2.00827300	4.49770600				
												H	2.23214600	2.58938800	2.95196600				
												C	-1.01114100	1.74488100	3.84715500				
												H	-1.88673000	1.31002800	3.36412700				
												H	-0.70849100	1.08668300	4.67017500				
												H	-1.30532500	2.70892300	4.27763100				
												C	-0.64907800	2.50118000	-2.25234500				
												H	-0.74334200	1.42054300	-2.27120300				
												C	-1.90671000	3.09375100	-2.91422600				
												H	-2.20740800	2.47068100	-3.76359800				
												H	-2.74641400	3.16010800	-2.21770900				
												H	-1.71375900	4.10021100	-3.30183400				
												C	0.56972300	2.87242700	-3.10079600				
												H	0.78132600	3.94584000	-3.02598700				
												H	1.45833500	2.32427800	-2.79522100				
												H	0.36869400	2.63772900	-4.15208400				
												C	2.59896800	-0.89741000	4.46690700				
												H	2.36127500	-0.09386300	5.17234100				
												H	1.69901900	-1.49729300	4.31691700				
												H	3.36694900	-1.53088600	4.92419400				

Figure 1S**.** Molecular structure of guanidine **3a**

Single crystals were obtained by slow evaporation at room temperature from a solution of **3a** in deuterated toluene. This compound has a 'CN_3' core and there are two different distances for the carbon-nitrogen bonds. The C1–N2 and C1–N3 distances are 1.357 (2) and 1.372 (2) Å, respectively, and these are consistent with the distances of a single carbon-nitrogen bond, whereas the C1–N1 distance of 1.305 (2) Å is closer to that of a double carbon-nitrogen bond. Some hydrogen atoms have been omitted for clarity.



Crystallographic Data for Compounds 1b, 2a, 3a

Single crystal X-ray Diffraction data for 3a

A clear colourless prismatic-like specimen of $C_{13}H_{21}N_3$, approximate dimensions 0.18 mm x 0.26 mm x 0.35 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1773 frames were collected. The total exposure time was 22.16 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 13122 reflections to a maximum θ angle of 25.33° (0.83 Å resolution), of which 2435 were independent (average redundancy 5.389, completeness = 100.0%, R_{int} = 2.45%, R_{sig} = 1.68%) and 2085 (85.63%) were greater than $2\sigma(F^2)$. The final cell constants of a = 14.1014(5) Å, b = 11.3796(5) Å, c = 8.7040(4) Å, β = 107.869(2)°, volume = 1329.34(10) Å^3, are based upon the refinement of the XYZ-centroids of 6062 reflections above 20 σ(I) with 4.693° < 2θ < 52.73°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.891.

The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9771 and 0.9881. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{13}H_{21}N_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 157 variables converged at R1 = 3.50%, for the observed data and wR2 = 11.89% for all data. The goodness-of-fit was 1.013. The largest peak in the final difference electron density synthesis was 0.265 e$^-$/Å^3 and the largest hole was -0.312 e$^-$/Å^3 with an RMS deviation of 0.119 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.096 g/cm^3 and F(000), 480 e$^-$.

Sample and crystal data for 3a.

Chemical formula	$C_{13}H_{21}N_3$	
Formula weight	219.33	
Temperature	210(2) K	
Wavelength	0.71073 Å	
Crystal size	0.18 x 0.26 x 0.35 mm	
Crystal habit	clear colourless prismatic	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 14.1014(5) Å	α = 90°
	b = 11.3796(5) Å	β = 107.869(2)°
	c = 8.7040(4) Å	γ = 90°
Volume	1329.34(10) Å^3	
Z	4	
Density (calculated)	1.096 Mg/cm^3	
Absorption coefficient	0.067 mm^{-1}	
F(000)	480	

Data collection and structure refinement for 3a.

Theta range for data collection	1.52 to 25.33°	
Index ranges	-16<=h<=16, -13<=k<=13, -10<=l<=10	
Reflections collected	13122	
Independent reflections	2435 [R(int) = 0.0245]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9881 and 0.9771	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2435 / 0 / 157	
Goodness-of-fit on F^2	1.013	
Δ/σ_{max}	0.001	
Final R indices	2085 data; I>2σ(I)	R1 = 0.0350, wR2 = 0.0957
	all data	R1 = 0.0484, wR2 = 0.1189
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0654P)^2+0.4029P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.265 and -0.312 eÅ^{-3}	
R.M.S. deviation from mean	0.119 eÅ^{-3}	

Single crystal X-ray Diffraction data for 1b

A clear colourless prismatic-like specimen of $C_{28}H_{15}BF_{15}N$, approximate dimensions 0.22 mm x 0.36 mm x 0.39 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1722 frames were collected. The total exposure time was 2.39 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 43375 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 4860 were independent (average redundancy 8.925, completeness = 99.9%, R_{int} = 3.05%, R_{sig} = 1.72%) and 3940 (81.07%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.7816(3) Å, b = 17.0803(4) Å, c = 14.4528(4) Å, β = 93.7450(10)°, volume = 2655.84(12) $Å^3$, are based upon the refinement of the XYZ-centroids of 9958 reflections above 20 σ(I) with 4.573° < 2θ < 51.21°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.911. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9366 and 0.9635.
The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with Z = 4 for the formula unit, $C_{28}H_{15}BF_{15}N$. The final anisotropic full-matrix least-squares refinement on F^2 with 409 variables converged at R1 = 4.83%, for the observed data and wR2 = 15.70% for all data. The goodness-of-fit was 1.016. The largest peak in the final difference electron density synthesis was 1.000 $e^-/Å^3$ and the largest hole was -0.551 $e^-/Å^3$ with an RMS deviation of 0.082 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.654 g/cm^3 and F(000), 1320 e^-.

Sample and crystal data for ab.

Chemical formula	$C_{28}H_{15}BF_{15}N$	
Formula weight	661.22	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal size	0.22 x 0.36 x 0.39 mm	
Crystal habit	clear colourless prismatic	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 10.7816(3) Å	α = 90°
	b = 17.0803(4) Å	β = 93.7450(10)°
	c = 14.4528(4) Å	γ = 90°
Volume	2655.84(12) $Å^3$	
Z	4	
Density (calculated)	1.654 Mg/cm^3	
Absorption coefficient	0.170 mm^{-1}	
F(000)	1320	

Data collection and structure refinement for 1b.

Theta range for data collection	2.24 to 25.35°	
Index ranges	-12<=h<=12, -20<=k<=20, -17<=l<=17	
Reflections collected	43375	
Independent reflections	4860 [R(int) = 0.0305]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9635 and 0.9366	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4860 / 0 / 409	
Goodness-of-fit on F^2	1.016	
Final R indices	3940 data; I>2σ(I)	R1 = 0.0483, wR2 = 0.1378
	all data	R1 = 0.0618, wR2 = 0.1570
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0911P)^2+2.5447P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.000 and -0.551 $eÅ^{-3}$	
R.M.S. deviation from mean	0.082 $eÅ^{-3}$	

Single crystal X-ray Diffraction data for 2a

A clear colourless prismatic-like specimen of $C_{31}H_{21}BF_{15}N_3$, approximate dimensions 0.12 mm x 0.17 mm x 0.20 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1819 frames were collected. The total exposure time was 15.16 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The

integration of the data using a monoclinic unit cell yielded a total of 48626 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 5530 were independent (average redundancy 8.793, completeness = 100.0%, R_{int} = 3.89%, R_{sig} = 2.32%) and 4569 (82.62%) were greater than 2σ(F^2). The final cell constants of a = 10.9239(7) Å, b = 19.2190(11) Å, c = 14.3968(9) Å, β = 93.539(3)°, volume = 3016.8(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9928 reflections above 20 σ(I) with 4.548° < 2θ < 52.61°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.917. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9687 and 0.9810.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with Z = 4 for the formula unit, $C_{31}H_{21}BF_{15}N_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 455 variables converged at R1 = 3.11%, for the observed data and wR2 = 9.42% for all data. The goodness-of-fit was 1.001. The largest peak in the final difference electron density synthesis was 0.446 $e^-/Å^3$ and the largest hole was -0.335 $e^-/Å^3$ with an RMS deviation of 0.059 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.610 g/cm^3 and F(000), 1472 e^-.

Sample and crystal data for 2a.

Chemical formula	$C_{31}H_{21}BF_{15}N_3$	
Formula weight	731.32	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal size	0.12 x 0.17 x 0.20 mm	
Crystal habit	clear colourless prismatic	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 10.9239(7) Å	α = 90°
	b = 19.2190(11) Å	β = 93.539(3)°
	c = 14.3968(9) Å	γ = 90°
Volume	3016.8(3) $Å^3$	
Z	4	
Density (calculated)	1.610 Mg/cm^3	
Absorption coefficient	0.160 mm^{-1}	
F(000)	1472	

Data collection and structure refinement for 2a.

Theta range for data collection	1.77 to 25.35°	
Index ranges	-13<=h<=13, -21<=k<=23, -17<=l<=17	
Reflections collected	48626	
Independent reflections	5530 [R(int) = 0.0389]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9810 and 0.9687	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5530 / 0 / 455	
Goodness-of-fit on F^2	1.001	
Δ/σ_{max}	0.001	
Final R indices	4569 data; I>2σ(I)	R1 = 0.0311, wR2 = 0.0833
	all data	R1 = 0.0420, wR2 = 0.0942
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0550P)^2+1.3622P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.446 and -0.335 eÅ^{-3}	
R.M.S. deviation from mean	0.059 eÅ^{-3}	