C–C Activation

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Rhodium(I)-Catalyzed Decarbonylative Spirocyclization through C–C Bond Cleavage of Benzocyclobutenones: An Efficient Approach to Functionalized Spirocycles**

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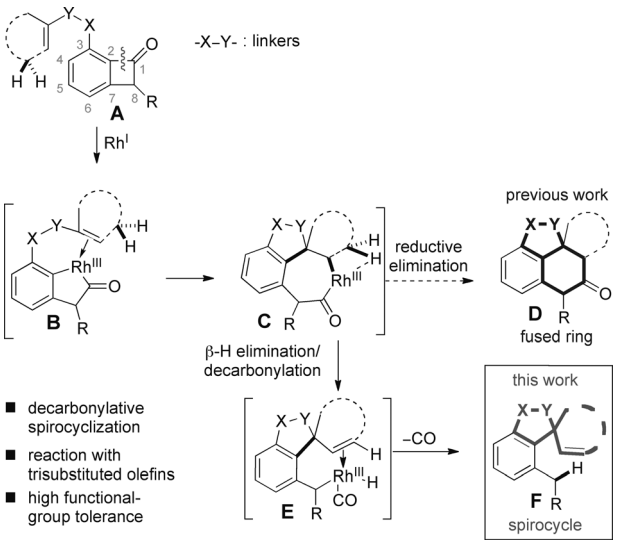
Dedicated to Professor Chul-Ho Jun on the occasion of his 60th birthday

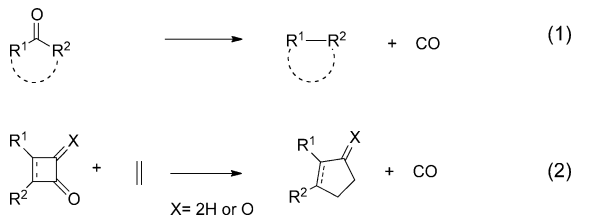
Abstract: *The rhodium-catalyzed formation of all-carbon spirocenters involves a decarbonylative coupling of trisubstituted cyclic olefins and benzocyclobutenones through C–C activation. The metal–ligand combination [{Rh(CO)$_2$Cl}$_2$]/P(C$_6$F$_5$)$_3$ catalyzed this transformation most efficiently. A range of diverse spirocycles were synthesized in good to excellent yields and many sensitive functional groups were tolerated. A mechanistic study supports a hydrogen-transfer process that occurs through a β-H elimination/decarbonylation pathway.*

Catalytic carbon–carbon bond (C–C) activation/functionalization provides a unique platform to develop novel transformations that are challenging using conventional approaches.[1] In particular, C–C activations that involve a decarbonylation process are of significant synthetic value because they allow the preparation of compounds that lack a carbonyl moiety from a more readily available ketone precursor.[2] Given the ubiquity of carbonyl compounds, the decarbonylative C–C activation followed by a C–C forming process would potentially offer a distinct synthetic strategy using carbonyl groups as a "traceless handle".

Although highly attractive, the decarbonylative C–C activation strategy has been largely limited to its reaction scope. Previous efforts primarily involved a direct CO extrusion to give the corresponding hydrocarbon products [Eq. (1)].[3,4] Only a few examples are known to engage the addition of simple olefins [Eq. (2)].[5] To broaden the scope and applicability of the decarbonylative C–C activation/functionalization strategy, new classes of synthetically useful transformations are highly sought. Herein we describe our development of a rhodium-catalyzed decarbonylative spirocyclization through an intramolecular coupling between olefins and benzocyclobutenones (Scheme 1), in which the reaction course can be controlled by the choice of the ligand on the metal catalyst.



Scheme 1. Rh^{I}-catalyzed decarbonylative coupling between olefins and benzocyclobutenones through C–C activation.



Recently, we developed a Rh-catalyzed intramolecular carboacylation between benzocyclobutenones and olefins.[6] This "cut and sew" transformation begins with the oxidative addition of Rh^{I} into the benzocyclobutenone C1–C2 bond, followed by migratory insertion into the olefin to give a 7-membered metallacycle (**C**), and subsequent reductive elimination to afford fused-ring systems (**D**). However, if a β-H elimination/decarbonylation process can be promoted instead of direct C–C reductive elimination, spirocycles containing all-carbon quaternary centers would be rapidly formed when

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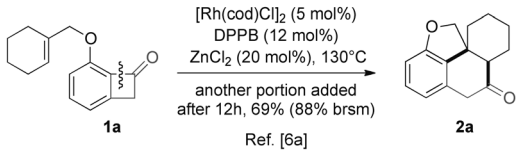
cyclic trisubstituted olefins were employed as the coupling partner (Scheme 1). Given that spirocycles are important structural motifs often found in bioactive natural products, whereas efficient synthesis of functionalized spirocycles has heretofore been challenging,[7] this decarbonylative C–C activation strategy would provide a complementary approach to the previous spirocyclization methods.[8] However, the challenge here is how one can promote the β-H elimination and decarbonylation instead of direct reductive elimination?

Previously, we discovered that bidentate phosphine ligands with a large bite angle promote the direct reductive elimination; however, a Lewis acid is needed to enhance the electrophilicity of the substrate to permit coupling with polysubstituted olefins [Eq. (3)].[6a] We hypothesized that the use of monodentate π-acidic ligands (inspired by a recent work of Tang[9]) would benefit the formation of the spirocycle in two different aspects: 1) the faster ligand exchange (compared to bidentate ligands) would facilitate the formation of open coordination sites on Rh, which in turn could favor both β-H elimination and CO deinsertion; 2) the more electron-deficient catalyst would coordinate more strongly with the trisubstituted olefins, thus enhancing subsequent migratory insertion.[10]

Previous results

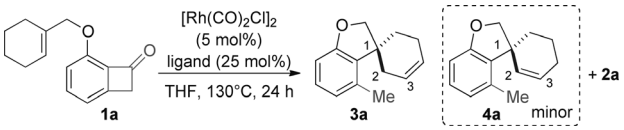


(3)

cod=1,5-cyclooctadiene; DPPB=1,4-bis(diphenylphosphino)butane

To test our hypothesis, compound **1a**, which previously gave the tetracyclic "cut and sew" product **2a** [Eq. (3)], was employed as the model substrate for the formation of the spirocycle. A number of Rh^I precatalysts and phosphine ligands were examined. Indeed, when electron-rich or bidentate ligands, such as PCy_3, dppb, and dppf, were employed, the desired decarbonylative spirocyclization product was not obtained; in contrast, use of the more electron-poor [$\{Rh(CO)_2Cl\}_2$] alone produced the 2*H*-benzofuran-[4.5]-spirocycle **3a** in about 3% yield (entry 1, Table 1). Use of an acac ligand on the Rh versus Cl was detrimental to the catalyst reactivity, leading to slight decomposition of **1a** (entry 2, Table 1). The in situ generated cationic Rh^I led to the dealkylation of **1a** to give 3-OH-benzocyclobutenone (entry 3, Table 1). Use of the more electron-rich PPh_3 or highly electron-deficient phosphites as the ligands completely shut down the catalyst reactivity (entries 4–6, Table 1). However, we found that employment of the π-acidic triarylphosphine ligands significantly promoted the formation of the desired spirocycle **3a** (entries 7–11, Table 1), among which the $P(C_6F_5)_3$ ligand proved to be most efficient. Finally, simply by lowering the ligand/metal ratio to 1:1, formation of the undesired reductive-elimination product (**2a**) was significantly inhibited; spirocycle **3a** was isolated as the major product in 72% yield (entry 10, Table 1). Presumably, when less ligand is present, the metal tends to provide open coordination sites for β-H elimination.[10] It is interesting to note that under these reaction conditions the C3 olefin isomer (after one "chain walk"[11]) of the spirocyclic product was selectively afforded (for a mechanistic study, see below).[12,13] Further lowering the ligand/metal ratio to 0.5:1 gave a similar result (entry 11, Table 1).

Table 1: Selected optimization conditions.



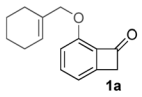
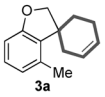
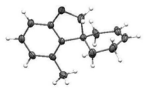
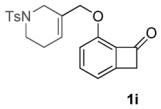
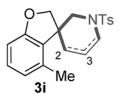
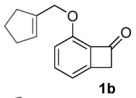
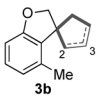
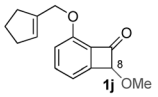
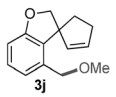
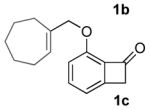
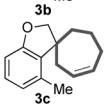
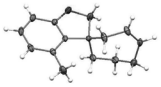
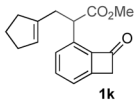
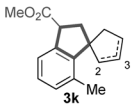
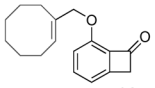
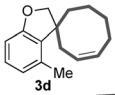
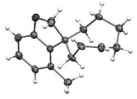
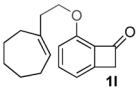
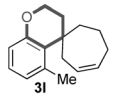
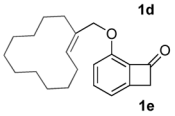
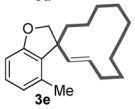
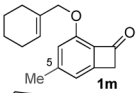
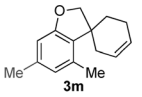
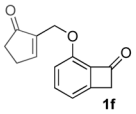
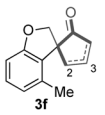
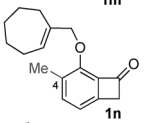
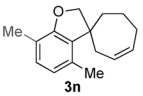
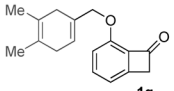
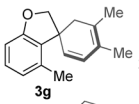
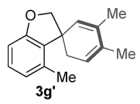
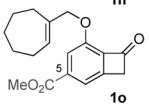
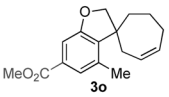
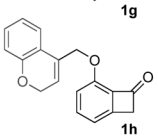
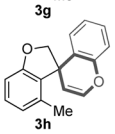
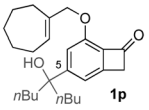
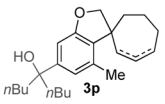
Entry	Precatalyst	Ligand/Additive	Yield [%][a] 3a/4a	2a
1	$[\{Rh(CO)_2Cl\}_2]$	none	3/<1%	2
2[b]	$[Rh(CO)_2(acac)]$	none	0	0
3[c]	$[\{Rh(CO)_2Cl\}_2]$	$AgSbF_6$ (10 mol%)	0	0
4	$[\{Rh(CO)_2Cl\}_2]$	PPh_3	0	0
5	$[\{Rh(CO)_2Cl\}_2]$	$P(OCH_2CF_3)_3$	0	0
6	$[\{Rh(CO)_2Cl\}_2]$	$P[OCH(CF_3)_2]_3$	0	0
7	$[\{Rh(CO)_2Cl\}_2]$	P(2-furyl)$_3$	7/≤4	22
8	$[\{Rh(CO)_2Cl\}_2]$	$P[3,5\text{-}(CF_3)_2C_6H_3]_3$	14/14	39
9[d]	$[\{Rh(CO)_2Cl\}_2]$	$P(C_6F_5)_3$	30/7	60
10[d,e]	$[\{Rh(CO)_2Cl\}_2]$	$P(C_6F_5)_3$	72[f]/≤4	22[f]
11[d,g]	$[\{Rh(CO)_2Cl\}_2]$	$P(C_6F_5)_3$	66/≤5	15

[a] Yields were determined by ^1H NMR spectroscopy using mesitylene as the internal standard. [b] 10 mol% $[Rh(CO)_2(acac)]$ was used. [c] 3-OH-benzocyclobutenone was isolated in 53% yield. [d] The reaction time was 36 h. [e] 10 mol% $P(C_6F_5)_3$ of the ligand was used. [f] Yields of isolated products. [g] 5 mol% $P(C_6F_5)_3$ was used. acac = acetylacetonates.

Next, the scope of this decarbonylative spirocyclization was investigated (Table 2). First, cyclic olefins with different ring sizes were examined. To our delight, 5-, 6-, 7-, 8-, and 12-membered ring substrates all underwent this transformation smoothly (entries 1–5, Table 2); a single olefin isomer was observed except in the case of the 5-membered ring substrate (entry 2, Table 2). Intriguingly, spirocyclization of the 12-membered ring substrate (**1e**) proceeded to give a *trans* olefin in 90% yield without further alkene isomerization (entry 5, Table 2). The enhanced reactivity of substrate **1e** is likely attributed to a transannular interaction caused by the 12-membered cycle.[14] The structures of spirocycles **3a**, **3c**, and **3d** were unambiguously confirmed by X-ray crystallography. Electron-deficient olefins, such as an enone, also reacted, albeit with a lower conversion (entry 6, Table 2). It is noteworthy that this spirocycle formation method is highly chemoselective and a variety of sensitive functional groups, including dienes, ketones, enamides, esters, benzyl and vinyl ethers, and unprotected tertiary alcohols are tolerated (entries 6–10, 15, and 16, Table 2), which is likely attributed to the near neutral reaction conditions. For example, when dihydrobenzopyran **1h** was employed as the substrate, the vinyl ether based spirocycle was isolated in 71% yield (entry 8, Table 2).

In addition, when the C8-methoxy-substituted benzocyclobutenone **1j** was utilized, the spirocycle containing a benzyl ether moiety (**3j**) was isolated in 59% yield as a single isomer (entry 10, Table 2). While the exact reason is

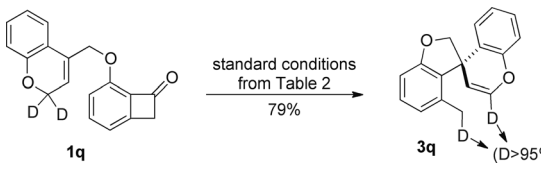
Table 2: Substrate scope.[a]

Entry	Substrate	Product/Yield[b]	Entry	Substrate	Product/Yield[b]
1	 **1a**	 **3a** 72% 	9[c]	 **1i**	 **3i** 67% $C_2 : C_3$ isomer = 3.2:1 (separable)
2[c]	 **1b**	 **3b** 78% $C_2 : C_3$ isomer = 1:1.7[f]	10	 **1j**	 **3j** 59% + **3b** (18%) $C_2 : C_3$ isomer = 1:1.7[f]
3	 **1c**	 **3c** 86% 	11[c,e]	 **1k**	 **3k** 57% $C_2 : C_3$ isomer = 1:1[f]
4	 **1d**	 **3d** 56% 	12	 **1l**	 **3l** 79%
5	 **1e**	 **3e** 90%	13	 **1m**	 **3m** 84%
6[c,d]	 **1f**	 **3f** 50% (82%) $C_2 : C_3$ isomer = 1:1.4 (separable)	14	 **1n**	 **3n** 67%
7[c]	 **1g**	 **3g** + 2.5 : 1[f] 65%  **3g'**	15	 **1o**	 **3o** 90%
8	 **1h**	 **3h** 71%	16	 **1p**	 **3p** 77% $C_2 : C_3$ isomer = 1: 6.3[f]

[a] Each reaction was run on a 0.2 mmol scale in a sealed vial, using 5 mol% $[\{Rh(CO)_2Cl\}_2]$ and 10 mol% $P(C_6F_5)_3$, in THF, at 130°C, for 36 h. [b] Yields of isolated products. [c] Ratios of olefin regioisomers were determined by ^{1}H NMR spectroscopy or were based on the yields of isolated products (see the Supporting Information for more details). [d] Numbers in parenthesis are yields based on recovered starting material (brsm). [e] Compound **3k** was characterized by a subsequent olefin hydrogenation (see the Supporting Information for details). [f] Isolated as inseparable isomers.

still unclear, the presence of the methoxy group at C8 likely promotes a faster C–H reductive elimination rather than olefin migration.[10] Interestingly, spirocycle **3b** was also isolated in 18% yield.[15] Furthermore, we discovered that, besides forming benzofuran-based products, other classes of spirocycles can also be efficiently synthesized: first, this transformation works well with substrates that lack an ether linkage (entry 11, Table 2); second, the cyclization that gives a 6-membered ring proceeded equally well to give benzopyrane-based spirocycle **3l** in 79% yield (entry 12, Table 2). Note that, except for substrates **1a**, **1i**, and **1m**,[16] the ("cut and sew") product of a direct reductive elimination was not observed for other substrates depicted in Table 2. In addition, substrates with different substituents at the C4 and C5 positions of the benzocyclobutenone also reacted smoothly in the spirocyclization (entries 13–16, Table 2).[17] It is encouraging to note that substrates bearing substituents with different steric and electronic properties, including methyl, 1-butyl-1-hydroxypentyl, and methyl ester groups, all provided good yields of the desired spirocycles.[17b]

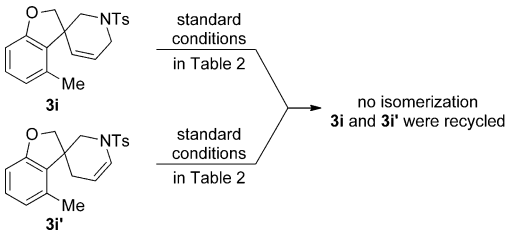
To provide mechanistic insights for this transformation, a deuterium-labeling experiment [Eq. (4)] was designed. Substrate **1n** was readily synthesized from propargyl alcohol and D_2-paraformaldehyde in five steps with an overall yield of 44% (for details, see the Supporting Information). By reacting **1n** under the standard decarbonylative spirocyclization conditions, spirocycle **3n** with more than 95% deuterium incorporation at the methyl group was isolated in 79% yield. This experiment strongly supports our hypothesis that this transformation includes a β-H elimination, decarbonylation, and then C–H reductive elimination pathway (see above, Scheme 1).



1q **3q** (4)

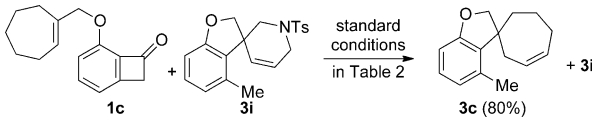
Another mechanistic problem regards the selective olefin chain walk with most substrates. We postulated that two reaction pathways are possible for the olefin migration: 1) alkene isomerization after the decarbonylative spirocyclization (that is, the C3 isomer comes from the C2 isomer), or

2) alkene isomerization during the decarbonylative spirocyclization (that is, the C3 and C2 isomers are formed independently). Compounds **3i** and **3i′** were chosen as the model compounds because they can be readily separated through column chromatography. When pure **3i** and **3i′** were subjected to the standard reaction conditions (shown in Table 2), no isomerization for either product was observed after 36 h [Eq. (5)], which indicates the $[\{Rh(CO)_2Cl\}_2]/P(C_6F_5)_3$ system cannot isomerize the alkene in the products.

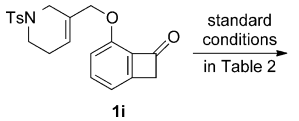


(5)

A cross-over experiment was also carried out to examine whether the intermediates generated in the catalytic cycle, for example, a Rh^{III}–H species, can isomerize the alkenes. Reaction of compounds **1c** and **3i** under the standard reaction conditions provided **3c** in 80% yield, but no isomerization of **3i** was found [Eq. (6)]. When the reactions of **1i** and **1b** were monitored separately over time, the ratio between the C2 and C3 isomers remained largely unchanged [Eqs. (7) and (8)], which is consistent with our earlier observation for substrate **1a**.[13] In combination with the deuterium-labeling experiment [Eq. (4)], these studies suggest that the olefin chain walk likely occurs during (instead of after) the process of the spirocycle formation, thus the C2 and C3 isomers are expected to form independently (not shown in Scheme 1).

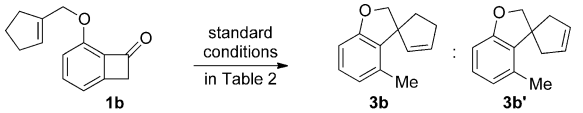


(6)



3i	:	3i'	:	1i	t [h]
1.0	:	0.28	:	2.0	12
1.0	:	0.29	:	0.24	24
1.0	:	0.27	:	0.03	36

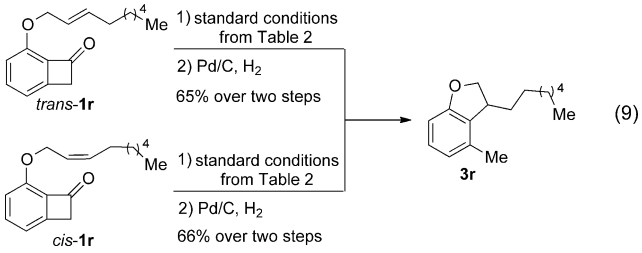
(7)



3b	:	3b'	:	1b	t [h]
1.0	:	1.75	:	0.61	12
1.0	:	1.73	:	0.19	24
1.0	:	1.72	:	0.02	36

(8)

Furthermore, we found this transformation is not limited to cyclic trisubstituted olefins, as the linear disubstituted olefins also underwent the decarbonylative cyclization to provide the cyclization products. While coupling of linear trisubstituted alkenes proved challenging,[18] reactions with the 1,2-disubstituted olefins proceeded smoothly [Eq. (9)].[19] It is interesting to note that the olefin geometry does not significantly affect the reactivity.



(9)

In conclusion, we have developed a Rh-catalyzed decarbonylative spirocyclization of olefins and benzocyclobutenones through C–C activation, which provides a complementary but distinct way to generate all-carbon spirocenters. This reaction exhibits several key features. First, it operates at near neutral reaction conditions, and therefore tolerates many acid- or base-sensitive functional groups, which represents a major advantage over classical spirocycle syntheses. Second, it has a broad substrate scope (both electron-rich and electron-poor olefins undergo the reaction), thus providing a range of structurally diversified spirocycles, which indicates great potential for application in the synthesis of complex molecules. Furthermore, to the best of our knowledge, this represents the only report that combines C–C activation, olefin insertion, β-H elimination, and decarbonylation in a one-reaction sequence. The unique mode of reactivity described here may provide broad implications for designing new tandem transformations. Further expansion of the substrate/reaction scope and the development of an enantioselective version of this reaction[20] are ongoing.

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Keywords: C–C activation · decarbonylation · homogeneous catalysis · rhodium · spirocycles

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[13] An attempt to capture the non-chain-walk intermediate (**4a**) under the reaction conditions (shown in entry 10, Table 1) was unfruitful. Even when the reaction was quenched at a low conversion, **3a** was observed as the dominant product.

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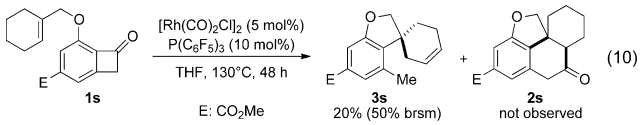
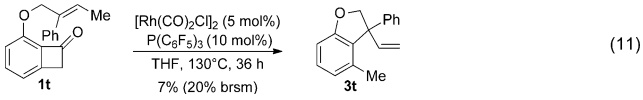
[15] The mechanism for the formation of **3b** is unclear.

[16] For substrate **1i**, the corresponding "cut and sew" product (**2i**) was isolated in 14% yield. For substrate **1m**, the corresponding "cut and sew" product (**2m**) was isolated in 12% yield.

[17] a) The C6-substituted substrate was challenging to prepare. b) The reaction of the C5-ester-substituted substrate **1s** has been attempted twice under the decarbonylative spirocyclization conditions [Eq. (10)]. The desired spirocycle was obtained, albeit in a lower yield with decomposition of the starting material (the exact reason is unclear).



[18] A linear trisubstituted olefin substrate (**1t**) was also synthesized and tested under the reaction conditions [Eq. (11)]. The desired decarbonylative cyclization product **3t** was obtained, albeit in a low yield (low conversion), which is likely due to the steric hindrance of the alkene group.



[19] The cyclization product from Equation (9) contains several olefin isomers.

[20] Not surprisingly, when monophos was employed as the chiral ligand for this transformation, the desired spirocyclization product was not observed (see above, entries 5 and 6, Table 1). Chiral monodentate electron-deficient triarylphosphines will be developed and investigated for the asymmetric transformation in due course.

[21] CCDC 962877 (**3a**), 962878 (**3c**), and 962879 (**3d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

