Controlled Alternating Metathesis Copolymerization of Terminal Alkynes

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ABSTRACT: Terminal alkynes display high reactivity towards Ru-carbene metathesis catalysts. However, the formation of a less reactive bulky carbene hinders their homopolymerization. Simultaneously, the higher reactivity of alkynes does not allow efficient cross propagation with sterically less hindered cycloalkene monomers resulting in inefficient copolymerization. Nonetheless, terminal alkynes undergo rapid cross-metathesis with vinyl ethers. Therefore, an efficient cross propagation can be achieved with terminal alkynes and cyclic enol ether monomers. Here, we show that terminal alkyne derivatives can be copolymerized in an alternating fashion with 2, 3-dihydrofuran using Grubbs' 3rd generation catalyst (**G3**). A linear relationship of the number average molecular weight *vs.* monomer to initiator ratio and block copolymer synthesis confirmed a controlled copolymerization. The SEC and NMR analyses of the synthesized copolymers confirmed the excellent control over molecular weight and exclusive alternating nature of the copolymer. The regioselective chain transfer of **G3** to vinyl ether and the high reactivity of Fischer type Ru carbene towards terminal alkynes was also exploited for polymer conjugation. Finally, the presence of an acid labile backbone functionality in the synthesized alternating copolymers allowed complete degradation of the copolymer within a short time interval which was confirmed by SEC analyses.

Ring opening metathesis polymerization (ROMP) offers a wide variety of functional monomers for microstructure controlled complex polymer design.[1,2,3,4,5] Moreover, the mild reaction conditions and vast functional group tolerance of the metathesis polymerizations also allow the incorporation of labile/degradable functionalities into the backbone for tunable degradability.[6,7,8,9,10,11] Therefore, ROMP became a common choice of polymerization among polymer chemists.

The release of ring strain is the driving force for ROMP polymerization. As such, highly strained cyclic monomers like norbornene, cyclopropene, cyclobutene, and cyclooctene derivatives are logical choices for metathesis polymerizations.[12] However, the sequence controlled incorporation of such strained monomers throughout the polymerization is challenging. Nonetheless, progress has been made regarding the sequential arrangements of such strained monomers during polymerization mainly in an alternating fashion.[13,14,15,16,17,18] The groups of Sampson, Xia, and our group developed alternating ROMP(AROMP) strategies based on the single molecular addition of highly strained cyclobutene, cyclopropene and oxanorbornene derivatives.[19,20,21,22,23,24,25,26]

Strategies have also been developed for sequence controlled ROMP polymerization of low-strained monomers.[27,28,29,30,31,32,33,34,35,36] Amongst these, tandem ring-opening ring-closing enyne metathesis has been studied most.[37,38,39,40,41,42] Even though, the alkyne undergoes spontaneous metathesis polymerization via an intramolecular tandem/cascade process, the intermolecular homo or copolymerization of such alkyne derivatives with Ru-based metathesis catalysts is still out of reach.

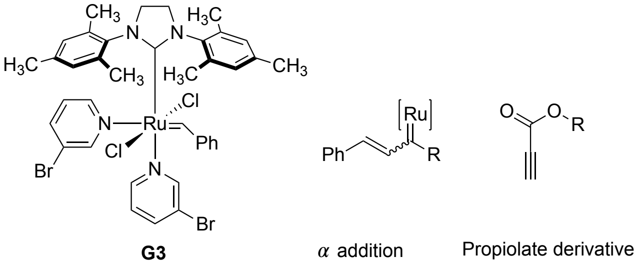
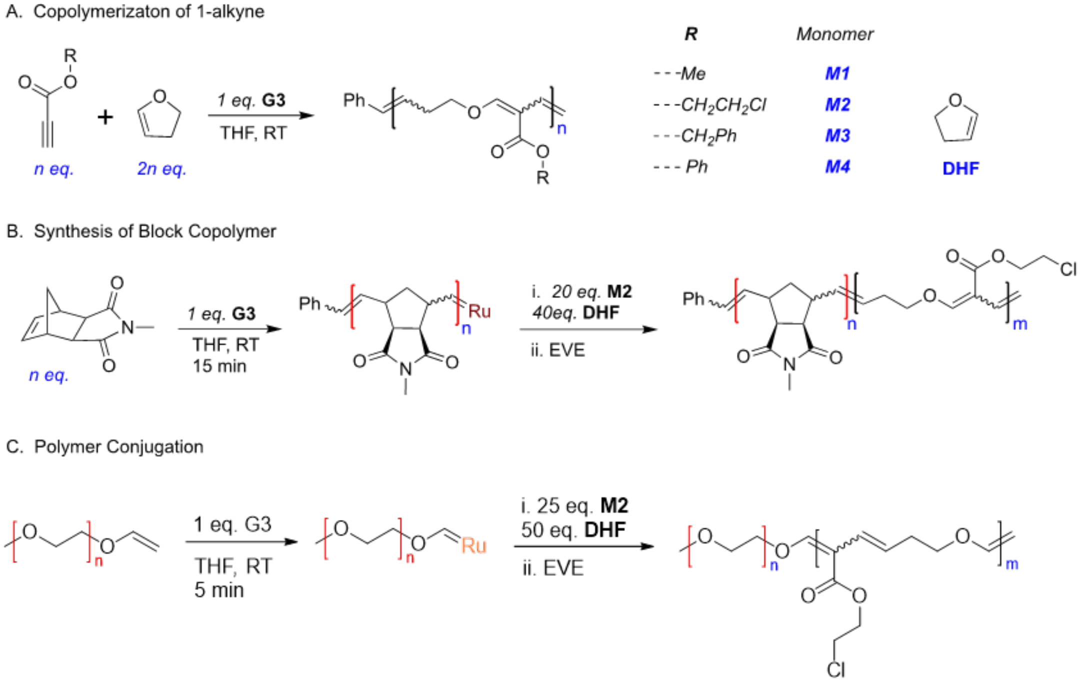


Figure 1. Grubbs' 3rd generation catalyst (G3) (left). Alpha addition of Ruthenium catalyst to terminal alkyne (center). Propiolate derivatives (right).

The ruthenium based Grubbs' type initiators undergo rapid alpha addition with 1-alkyne derivates resulting in a sterically hindered 1,1 disubstituted ruthenium carbene with diminished metathesis reactivity (Fig 1).[43,44,45,46] Moreover, the increasing double bond conjugation in the backbone further reduces the metathesis reactivity of Ru carbene complexes.[47,48] Consequently, homopolymerization of 1-alkynes becomes increasingly difficult. However, such extended conjugations can be avoided if

Scheme 1. General representation of alkyne copolymerization



alkynes can be copolymerized in an alternating fashion with another comonomer. Simultaneously, an alternating copolymerization of alkynes with sterically less hindered comonomers can overcome the steric restrains of the 1,1-disubstituted ruthenium carbene complex formed during metathesis polymerization of alkynes.[19,20,21] Unfortunately, due to the higher reactivity of 1-alkynes towards Ru carbene complexes and the formation of a less reactive bulky carbene complex, comonomers that can undergo cross propagation with 1-alkynes are scarce.

The Grubbs' benzylidene and alkylidene complexes undergo rapid regioselective cross metathesis with electron rich vinyl ether derivatives.[49,50,51,52,53] The resulting electron rich Fischer-type Ru carbene complexes are thermodynamically more stable and show much lower metathesis reactivity than Schrock-type Ru alkylidene complexes.[49] However, the less reactive Fischer-type Ru complexes are still capable of initiating the metathesis polymerization of highly reactive monomers.[54,55,56,57,58,59] In 2003, the Diver group reported that 1-alkynes undergo rapid intermolecular cross metathesis with vinyl ethers in the presence of Ru carbene complexes in excellent yield.[60,61] This indicates that an efficient chain transfer is happening from the propagating alkyne to the vinyl ether. As such, cyclic enol ethers could be efficient comonomers for the copolymerization of 1-alkynes. Even though terminal alkynes were reported to react in a cross metathesis reaction with vinyl ethers, the copolymerization of such alkynes with cyclic enol ethers has not yet been reported.

Here, we report the synthesis of a degradable alternating copolymer of 1-alkynes and DHF initiated with Grubbs' 3rd generation catalyst (**G3**) (Fig 1). Furthermore, the strict regioselective reaction of **G3** with vinyl ethers and the high reactivity of Ru-Fischer carbenes towards alkynes was also exploited to synthesize block copolymers from a vinyl ether terminated poly(ethylene glycol).Cyclic low strain enol ethers like DHF undergo homopolymerization in bulk or at high monomer concentrations.[57] The homopolymerization of such monomers can be avoided at lower monomer concentrations (<0.2M). In contrast, terminal alkynes rapidly react with Grubbs' 3rd generation catalyst (**G3**) yielding a less reactive bulky Schrock type alkylidene complex, resulting in inefficient homopolymerization.[43,44,46] Nonetheless, the Schrock type ruthenium carbene can undergo rapid exchange with the vinyl ether to form an energetically more stable Fischer-carbene.[49] Although the ruthenium Fischer-carbenes are less reactive, they successfully undergo cross propagation with a reactive substrate like a terminal alkyne.[60,61]

Therefore, DHF was considered as comonomer to copolymerize with propiolate derivatives (Fig 1). Thereafter, ^{1}H NMR experiments were used to study control over molecular weight and microstructure of homopolymerization of DHF and

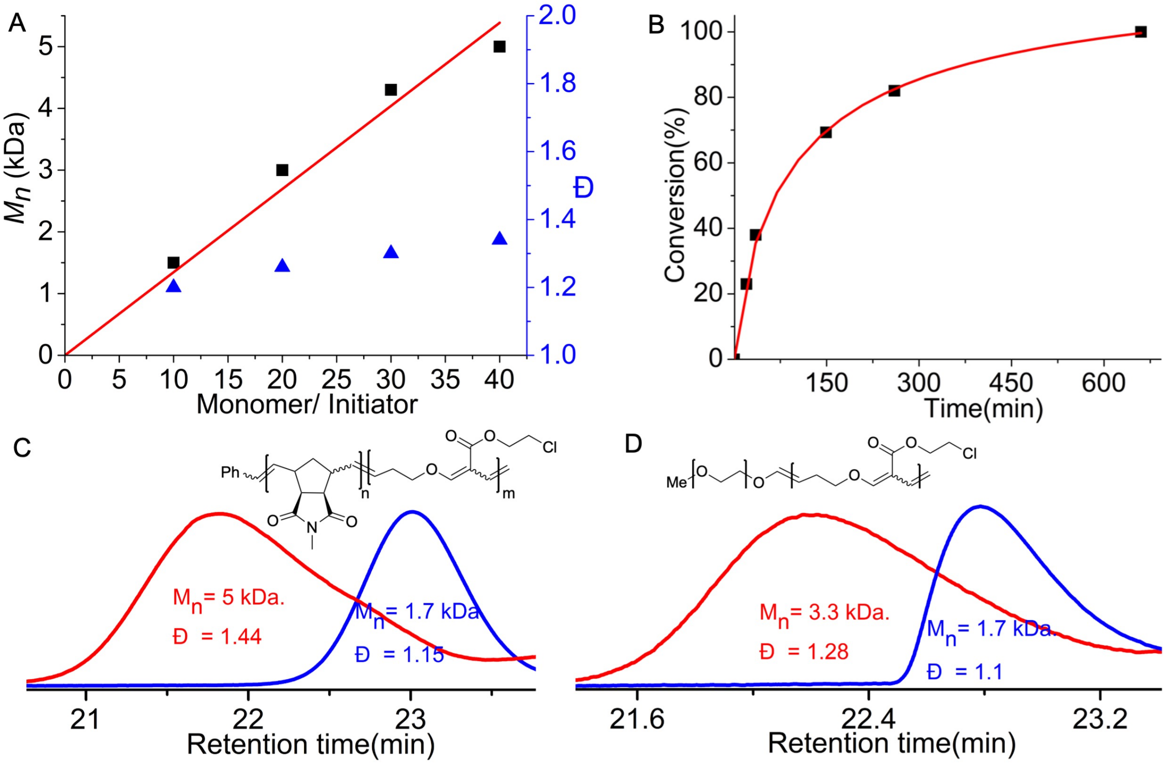


Figure 2. A. Plot of number average molecular weight vs monomer to initiator ratio for the copolymerization of **M1** and DHF (1:2) using **G3** with a DHF concentration of 0.14 M. B. Plot of **M1** conversion *vs.* time in a copolymer of **M1** and **DHF** (1: 10) with 5 mol% **G3** in THF-d8. C. SEC analysis for the block copolymer (**PB1**). D. SEC analysis for polymer conjugate **PB2** initiated from PEG vinyl ether macroinitiator.

methyl propiolate (**M1**). Interestingly, no significant homopolymerization was observed when **M1** was reacted with 3.3 mol% **G3** in THF-d$_8$ over 12h (see Fig S1). In a similar homopolymerization study of DHF (0.27M) with 3.3 mol% **G3** in THF-d$_8$, less than 20% DHF consumption was observed over 24h. However, a SEC analysis of the reaction mixture did not show any oligomer/polymer formation.

Next, to test our hypothesis that 1-alkynes can be copolymerized with DHF, another ^{1}H NMR copolymerization experiment was performed with **M1** (1eq), DHF (10eq), and 5 mol% **G3** in THF-d$_8$ (Scheme 1A, see Fig S2). The DHF concentration was kept below the equilibrium concentration of homopolymerization (<0.27M) to avoid homopolymerization of DHF. Surprisingly, a fast consumption of each monomer was observed during the initial course of the reaction and within 4 hours, 80% of **M1** conversion was achieved (Fig 2B, Fig S2). A SEC measurement of the precipitated polymer (**P1;** Mn$_{\text{(theoret.)}}$= 3.1 kDa.; Mn$_{\text{(SEC THF)}}$= 4 kDa.; Đ= 1.5) indicated a good control over molecular weight. Next, the alternating character of the synthesized polymer **P1** was analyzed by ^{1}H NMR spectroscopy. A comparison of the ^{1}H NMR spectrum of **P1** and polyDHF shows a characteristic shift in olefinic signals representing the alternating diad (see Fig 3, Fig S4). However, a significant extent of DHF homopolymeric signal was also detected (60 % alternating diad, Fig S19).

To overcome the oligomerizations of DHF, a similar ^{1}H NMR copolymerization experiment of **M1** and DHF was performed with lower DHF equivalents (M1:DHF=1:2) with 5 mol% **G3** (see table S1). Surprisingly, only 80% **M1** consumption was observed within 4 hours and remained unchanged even at extended reaction time. ^{1}H NMR analysis of the synthesized copolymer (**P2**; Mn= 6.5 kDa.; Đ= 1.6) showed a significant improvement in alternating character. However, a SEC measurement of the crude reaction mixture showed a poor control over molecular weight and dispersity (See Table S1). We believe that at lower DHF concentration **M1** undergoes homopropagation, resulting in catalyst deactivation and hence poor control over molecular weight. Next, **M1** (1eq) and DHF (2eq) were copolymerized with 5 mol% **G3** in THF-d$_8$ at 0.14M DHF concentration and followed by ^{1}H NMR spectroscopy. Interestingly, over 90% monomer conversion was achieved within 4.5 hours (Scheme 1A, see Fig S3). Simultaneously, a SEC measurement of the crude reaction mixture indicated good control over molecular weight with narrow dispersity (see Table S2). ^{1}H NMR analysis of the synthesized copolymer (**P3**; Mn= 3.2 kDa.; Đ= 1.2) confirmed the exclusive alternating nature of the copolymer (Fig 3). We therefore performed a set of copolymerizations using **M1** and DHF with varying monomer to **G3** ratios in THF (see table S1). A linear relationship between the number average molecular weight and monomer to initiator ratio with narrow dispersities was obtained (Fig 2A). The excellent molecular weight control (DP up to 50)

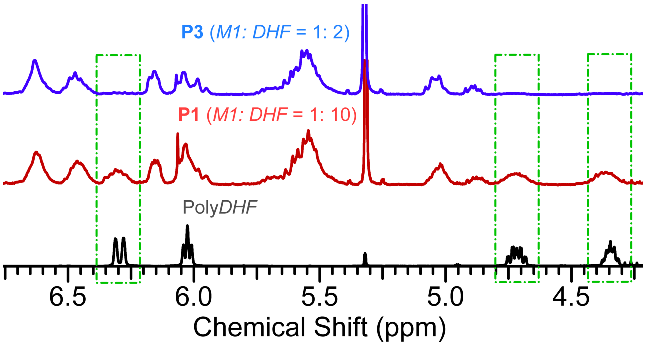


Figure 3. Stacked 1H NMR comparison of polyDHF, **P1** (1:10 **M1** and DHF), and **P3** (1:2 **M1** and DHF). The highlighted characteristic signals of polyDHF are compared with synthesized copolymer.

and exclusive alternating character of the synthesized copolymer were confirmed by SEC and ^{1}H NMR analyses (see SI).

Next, to test the versatility of the method, monomers **M2**, **M3** and **M4** were synthesized (see SI). Thereafter, **M2** was copolymerized with DHF in the presence of 10 mol% and 2.5 mol% of **G3** in THF at room temperature to obtain **P8** and **P9** respectively (see table S2). The SEC analyses of **P8** (Mn= 1.6 kDa.; Đ= 1.2) and **P9** (Mn= 7.1 kDa.; Đ= 1.3) confirmed an excellent control over molecular weight, while ^{1}H NMR analyses confirmed a highly alternating nature of the copolymer (see Fig S23). Then, monomer **M3** was copolymerized with DHF in the presence of 3.3 mol% **G3** to obtain **P10** (Mn= 6 kDa.; Đ= 1.4). Surprisingly, a copolymerization of monomer **M4** with DHF with 2 mol% **G3** shows much slower propagation rates than other monomers (**M1**-**M3**) tested here. We believe the higher steric bulk of **M4** caused the slower propagation. Nonetheless, SEC and NMR analysis of the synthesized copolymer **P11** (Mn= 9.4 kDa.; Đ= 1.4) confirmed a good control over molecular weight and high degree of alternation (see Fig S25).

Thereafter, the highly reactive phenylacetylene (**M5**) was also tested under optimized copolymerization conditions. Unfortunately, no polymer was obtained when phenylacetylene was copolymerized with 2 eq of DHF (0.14M) in THF. As mentioned earlier, we hypothesized that due to the higher reactivity of phenylacetylene cross propagation at lower DHF concentration was significantly reduced, resulting eventually in catalyst deactivation. However, such limitations can be overcome by increasing the DHF concentration. Interestingly, a quantitative conversion was observed when phenylacetylene (**M5**) was copolymerized with a ten-fold excess of DHF to obtain **P12** (Mn= 3 kDa.; Đ= 1.24, see Table S3). The copolymer **P13** (Mn= 11 kDa.; Đ= 1.52) was also synthesized with 2 mol% of **G3** in THF with a 1:10 phenylacetylene to DHF ratio. ^{1}H NMR analyses of the synthesized copolymers confirmed moderate degree of alternation (60% alternating diad), whereas SEC analysis confirmed control over molecular weight.

The possibility to form block copolymers is an important feature for any living polymerization. In our first experiment we investigated whether the monomer system **M2**/DHF could be used to extend a well-investigated polymer block prepared by ROMP. Therefore, *exo-N*-methylnorborneneimide (**MNI**) was polymerized with 8.3 mol% **G3** in THF for 15 min (Scheme 1B). Then, a mixture of **M2** and DHF was added to the polymerization solution and the progress of the reaction was followed by ^{1}H NMR spectroscopy. As expected, SEC measurements of the polymer before (Mn$_{\text{(1st block)}}$= 1.7 kDa.; Đ= 1.2) the addition of **M2**/DHF and after complete consumption of **M2** showed a distinct shift of the SEC trace, indicating the formation of a block copolymer (**PB1**; Mn$_{\text{(both blocks)}}$= 5 kDa.; Đ= 1.4) with excellent efficiency (Fig 2C). However, a minor amount of first block signal was also observed in the SEC of the final diblock copolymer.

While this experiment did not prove the living character of the **M2**/DHF system, it confirmed its controlled behavior even when macro-initiated from another polymer block.

NMR analysis of the synthesized copolymer also confirmed the formation of the block copolymer **PB1** (see Fig S28).

Next, a vinyl ether alkyne copolymerization was exploited for polymer conjugation. An efficient regioselective metathesis catalyst transfer to a polymer chain end is very challenging; especially, using Grubbs' 3rd generation (**G3**) catalyst.[62,63] However, Grubbs' catalysts undergo regioselective chain transfer with vinyl ethers with excellent efficiency. Therefore, Ru carbenes can be selectively converted to Fischer carbenes by reacting with a vinyl ether terminated polymer chain.[64] Thus, we believed that a chain extension could be achieved from a Fischer carbene macro initiator. To test the hypothesis, a vinyl ether end-functional PEG polymer was synthesized (Mn$_{\text{(macroinitiator)}}$= 1.7 kDa.; Đ= 1.1). Thereafter, the vinyl ether terminated PEG was treated with an equivalent amount of **G3** (Scheme 1C). An immediate measurement of a ^{1}H NMR spectrum showed a complete shift of the ruthenium benzylidene to the Fischer carbene complex (δ 13.53 ppm; see Fig S8). After that, a mixture of **M2** and DHF was added to the reaction mixture, and the progress of the reaction was followed by ^{1}H NMR spectroscopy. A SEC analysis after completion of the copolymerization showed a significant shift in SEC trace compared to the PEG macroinitiator (Fig 2D) and confirmed the formation of a block copolymer **PB2** (Mn$_{\text{(both blocks}}$= 3.3 kDa.; Đ= 1.3). Very few alternative methods are currently available to macro-initiate a metathesis polymerization from a polymeric end-group.[65]

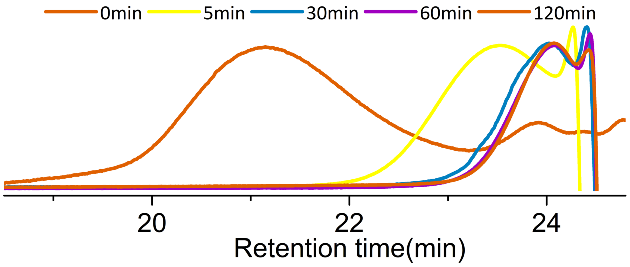


Figure 4. SEC analyses for degradation of **P10** under acidic condition.

While macro-initiated block copolymer formation works very well for our propriolate/DHF system, one major limitation observed in our polymerization system is the synthesis of block copolymers by sequential addition of different propriolates (for instance, **M1**, DHF followed by **M2**, DHF). The underlying reason could be the decomposition of propagating Ru complex when monomer concentration is low during the later stage of the polymerization as reported for alkyne polymerizations before.[66]

To demonstrate this peculiar non-living behavior we compared the controlled polymerization of **M1** and DHF with a target DP of 40 (all monomer added in one portion, see P7, Table S2) with the sequential addition of **M1**/DHF in two portions (each corresponding to a DP of 20). While a controlled polymerization was observed in the first experiment, the second resulted in an uncontrolled polymerization of the second block (see Fig S9). This limitation of the polymerization procedure is currently under investigation.

A microstructure controlled functional polymer with tunable degradability would fulfill the current demand of material chemists.[67,68] The copolymer synthesized from alkyne and DHF contains a highly acid labile backbone functionality. Hence, a complete degradation can be achieved under acidic conditions. To test the chemical degradability of the synthesized copolymer, a solution of polymer **P10** (Mn= 6 kDa.; Đ= 1.4) in DCM was treated with a 1:1 mixture of water and trifluoroacetic acid (see SI). The progress of the degradation was followed by SEC (Fig 4). Interestingly, a drastic reduction in molecular weight was observed within 5 min, and a complete degradation was achieved within 1 hour.

In conclusion, we have shown that 1-alkynes can be copolymerized with cyclic enol ethers in an alternating manner with a Grubbs' type initiator. An excellent degree of alternation can be achieved when propiolate derivates are copolymerized with DHF at low concentrations. A linear relationship between number average molecular weight and monomer to initiator ratio as well as successful macroinitiations to yield block copolymers confirmed the controlled nature of the polymerizations. Simultaneously, a new protocol for metathesis polymer conjugation was also established for the first time through regioselective chain transfer of **G3** to polymeric vinyl ether end groups. The higher reactivity of the Fischer carbene towards alkynes allows the synthesis of block copolymers from a macro initiator. Finally, the availability of acid labile functionality in the alternating copolymer backbone allows complete degradation of the functional polymer under acidic conditions. We believe the understanding of the reactivity of alkynes and the possibility of alternating copolymer synthesis provides a new pool of functional monomers in the toolbox of metathesis polymerization.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Instrument's data, Experimental methods, NMR data, MALDI-ToF data, SEC data and HRMS data. (PDF)

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Notes

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Graphical abstract: