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Convenient Route To Initiate Kumada Catalyst-Transfer Polycondensation Using Ni(dppe)Cl$_2$ or Ni(dppp)Cl$_2$ and Sterically Hindered Grignard Compounds

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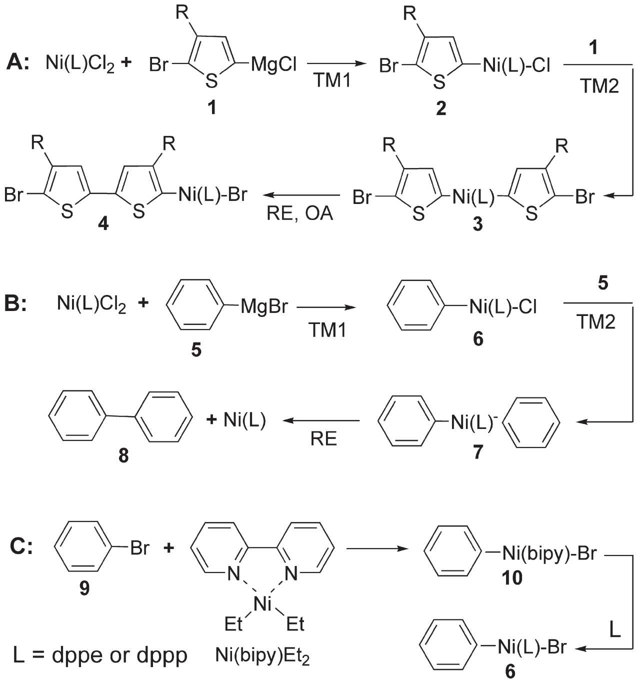
Scheme 1. (A) In Situ Formation of Ni Initiators from Commercially Available Ni(L)Cl$_2$ (Ni(dppe)Cl$_2$ or Ni(dppp)Cl$_2$) under GRIM Polymerization Conditions; (B) Failure of Attempts To Apply a Similar Strategy in the Preparation of Externally Added Initiators from Ni(L)Cl$_2$ and Phenylmagnesiumbromide (5);[a] (C) Highly Efficient Method for the Preparation of Initiators from Aryl Halides and Ni(bipy)Et$_2$ Followed by Ligand Exchange Using the Previously Reported Method[11] [b]



[a] This is due to the fact that the consecutive second transmetalation proceeds faster than the first one. [b] Key: TM, transmetalation; RE, reductive elimination; OA, oxidative addition; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,2-bis(diphenylphosphino)propane.

Conjugated polymers (CPs) attract considerable attention as promising materials for solar cells, field effect transistors, light-emitting diodes, etc.[1] However, the properties of existing CPs that are prepared predominantly by conventional step-growth polycondensations are still far from optimal. For industrial-scale applications, CPs with controllable molecular weight (MW), MW distribution, chain-end functionality, minimum amounts of defects, and as a result, controlled and reproducible optoelectronic properties are required. In addition, new CP architectures are needed that predictably self-assemble into desirable nanomorphologies, thus solving a longstanding problem with improper morphologies of active layers in optoelectronic devices.[1] Nowadays, chain-growth Kumada catalyst transfer polycondensations (KCTP), also referred to as Grignard metathesis polymerization (GRIM),[2] has become a powerful tool for the synthesis of well-defined polymers,[3] all-conjugated block copolymers[4] and polymer brushes.[8−10] However, despite impressive progress, several important challenges still remain. Although a number of model thiophene-based conjugated block copolymers were already synthesized via the sequential polymerization of different monomers,[4a−e] examples of all-conjugated block copolymers composed of two substantially different blocks remain scarce.[4f−i] While some effort has been made in synthesizing various types of donor−acceptor block copolymers,[5] all-conjugated block copolymers composed of state-of-the-art electron-donor and electron-acceptor conjugated blocks have not been synthesized to date. Such architectures are potentially promising materials for interface engineering in organic solar cells, especially when considering that power conversion efficiencies of all-polymer blend photovoltaics are currently lagging behind polymer/fullerene derivative-based devices.[6] Difficulties in preparing such block copolymers originate from the synthetic requirements that the two different blocks should be formed with the aid of the same catalyst, under approximately the same polymerization conditions and without a sacrifice in the chain-growth polymerization performance.[7] One way to solve this problem is to optimize the polymerization conditions and catalysts that are suitable to grow both blocks.[4f−i] An alternative strategy implies that two blocks are polymerized in two steps under conditions optimal for polymerization of each block.[8] Here, the most challenging step is to selectively prepare functional Ni-initiators in high yield (frequently called as externally added initiators) that are properly attached to molecules or objects, from which polymerization of conjugated polymer can finally be performed.[9−11] In usual GRIM polymerizations the Ni-initiator **4** is formed in situ from the first two monomer molecules **1** that react with Ni(dppe)Cl$_2$ or Ni(dppp)Cl$_2$ via intermediates **2** and **3** (Scheme 1A). The growing popularity of the GRIM polymerization method is, to a large extend, promoted by the convenient procedure for the preparation of commercially available and environmentally stable (to air and moisture) Ni(L)Cl$_2$. However, the preparation of functionalized initiators from Ni(L)Cl$_2$ remains challenging. Considering the reaction shown in Scheme 1A, one could assume that

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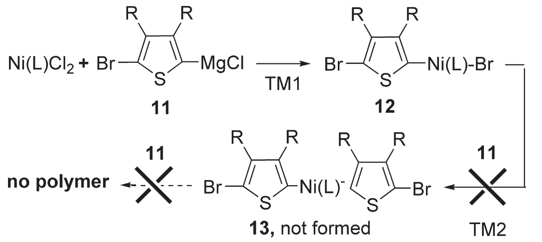
Scheme 2. Polymerization of Monomers Having Alkyl Substituents *ortho* to the Magnesium Atom (e.g., 11) Is Prohibited Due to Steric Hindrance Occurring in the Second Transmetalation Step (TM2)



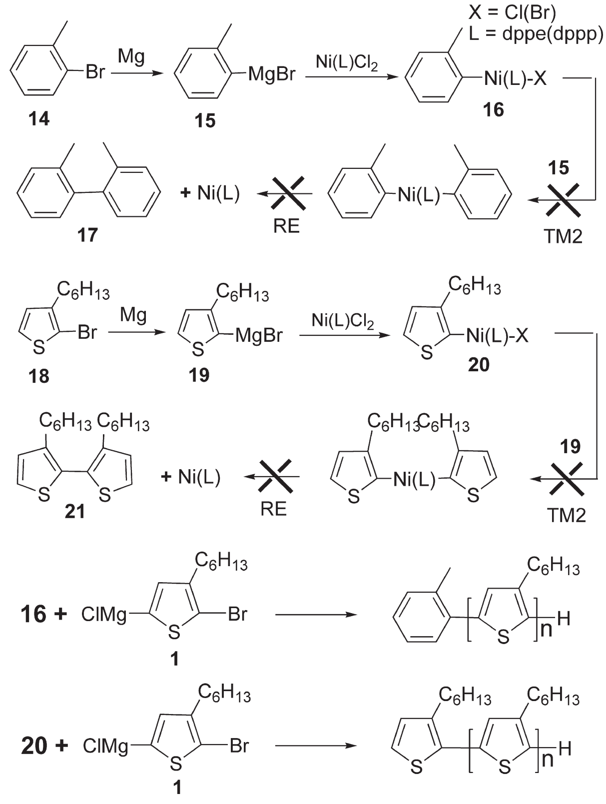
functionalized Ni-initiators can be prepared in a similar way via monotransmetalation of Ni(L)Cl$_2$ and readily available Grignard reagents, e.g., **5** (Scheme 1B). One should, however, take into account that product **6** forming in the first transmetalation step may undergo further transmetalation with **5** leading to **7** and finally to homocoupling product **8** and free Ni(0) species. Unfortunately, this unwanted pathway indeed dominates when Ph−MgBr is used as the Grignard reagent, as was demonstrated in our previous work.[10] Although a small amount of the potential initiator **6** was detected in the reaction mixture, the selectivity toward that species was generally low even at a high excess of Ni(L)Cl$_2$. The main reason for the low selectivity is the much better solubility of **6** compared to Ni(dppe)Cl$_2$, so that effectively **6** is always present in the reaction mixture in excess and reacts faster with **5**.

Since we faced severe problems in the preparation of initiators from Ni(L)Cl$_2$ and Grignard precursors via the transmetalation route as shown in Scheme 1B, we switched our attention to an alternative approach based on the oxidative addition of Ni(0) complexes to aryl halides. Unfortunately, Ni(0) complexes with two bidentate phosphorus ligands (e.g., Ni(dppp)$_2$ or Ni(dppe)$_2$) are inert toward aryl halides, and in situ generated Ni(dppp) or Ni(dppe) species supported by single ligands are too reactive to selectively give the desirable adducts. We therefore developed a method for the preparation of initiators via oxidative addition of Ni(0) carrying monodentate ligands (Ni(PPh$_3$)$_4$) to aryl halides Ar−X and reported the first surface-initiated polymerization of poly(3-hexylthiophene) (P3HT).[9] This process, however, suffers from two major drawbacks. First, initiators are formed in relatively low yields due to undesirable homocoupling side-reactions. Second, the chain-growth performance of the Ni(PPh$_3$)-catalyzed polymerization is much worse compared to Ni complexes with bidentate phosphorus ligands. While the latter problem can be circumvented using a ligand-exchange strategy,[12] the former is difficult to overcome and this strongly limits the applicability of the approach.

Recently, we developed a much more universal method[11] which is tolerant[13] to many functional groups and that allows a high-yield preparation of a large variety of initiators from differently substituted aryl halides (e.g., **9**, Scheme 1C). The method proceeds via intermediate bipyridyl (bipy)-supported complexes (e.g., **10**) formed from aryl halides and Ni(bipy)Et$_2$, which are further converted into dppp or dppe-based initiators via ligand-exchange (e.g., **6**).[14] However, Ni(bipy)Et$_2$ is not commercially available and highly reactive toward moisture and oxygen making it difficult to handle (a glovebox is usually required).

Very recently, we studied the reactivity of alkyl-substituted thiophenic monomers, such as 2-bromo-5-chloromagnesio-3,4-dihexylthiophene (**11**), and found that monomers having the alkyl substituent in the "*ortho*"-position to the chloromagnesium group do not polymerize if Ni(dppe)Cl$_2$ or Ni(dppp)Cl$_2$ catalysts are used (Scheme 2).[15] A closer look at the reaction products by in situ ^{31}P NMR measurements[16] revealed that these monomers participate in the first transmetalation step (TM1) with Ni(dppe)Cl$_2$ forming **12**, but are not reactive toward the consecutive second transmetalation step (TM2). Therefore, intermediate **13**, in which two alkyl substituents are directed toward the Ni center, is not formed, presumably because of steric hindrance occurring upon the attack of the second monomer onto **12**. We assumed such a behavior, which is unwanted if one aims to polymerize **11**, to be useful for the preparation of Ni-initiators starting from Ni(L)Cl$_2$.

Scheme 3. Preparation of Ni Initiators from Ni(L)Cl$_2$ and Sterically Hindered Grignard Compounds and Their Utilization in KCTP



To verify this idea, Grignard compounds **15** and **19** were prepared from *o*-bromotoluene **14** and 2-bromo-3-hexylthiophene **18**, respectively, and magnesium turnings (Scheme 3). These were then reacted with Ni(dppe)Cl$_2$ and Ni(dppp)Cl$_2$ at 0 °C in THF-d_8 and the reactions were followed by in situ ^{31}P NMR. In each case the first spectrum taken about 3 min after mixing (Figure 1) shows the major signals of the expected product of monotransmetalation **16** and **20**, respectively, represented by the corresponding bromo- and chloro-derivatives.

The formation of the bromo-derivatives results from the exchange of the chlorine atom from Ni(L)Cl$_2$ by bromide, which comes from MgBrCl (TM1 byproduct). Complete conversion of the chloro compound to the bromo-derivative was realized by the addition of a small amount of MgBr$_2$·Et$_2$O solution in THF-d_8, thus proving the signal assignment. Trace amounts of Ni(dppe)$_2$ and Ni(dppp)$_2$ side-products (1−2%) were also detected in the reaction mixtures. The composition of the reaction mixture remained constant for more than 30 min as long as no excess of the Grignard compound wass used. Further evidence for the Cl→Br exchange and the ^{31}P NMR assignments is provided by the additional synthesis of complex **20** starting from **18** via Scheme 1C,[11] which results in the direct formation of the bromo-complex. The identity with the complex formed from **19** and Ni(dppe)Cl$_2$ was confirmed by ^{31}P NMR (Supporting Information, Figure S2).

To carry out the polymerization, initiators **16** (or **20**) were prepared in situ by stirring **15** (or **19**) with equimolar amounts of

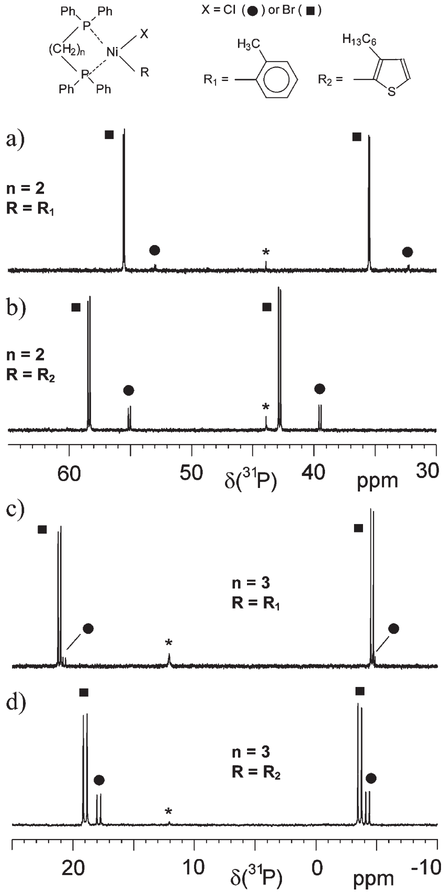


Figure 1. 202 MHz ^{31}P NMR spectra recorded about 3 min after the addition of **15** (a,c) and **19** (b,d) Ni(dppe)Cl$_2$ (a, b) and Ni(dppp)Cl$_2$ (c, d) in THF-d_8 at 0 °C. The full circles mark the two doublets of the products of monotransmetalation (X = Cl), i.e., **16-dppe** (a), **20-dppe** (b), **16-dppp** (c), **20-dppp** (d). The corresponding bromo-derivatives (X = Br;) formed by Cl → Br exchange are marked by full squares. The signals of the byproduct Ni(dppe)$_2$ (a, b) and Ni(dppp)$_2$ (c, d) are marked by an asterisk.

Ni(dppe)Cl$_2$ at 0 °C for 5 min, and then the resulting mixtures were added to solutions of **1**. Polymers carrying the corresponding aryl groups of the initiators were obtained with an initiation efficiency close to unity as evidenced by a good integration of starting and end groups in the ^{1}H NMR spectra and additionally by MALDI-TOF (Figures 2 and S1 (Supporting Infomation)). Overall, the observed polymerization result was practically identical to what we obtained with the same initiators prepared via the Ni(bipy)Et$_2$−based route,[11] but the preparation procedure of the initiators reported herein is much more convenient to conduct.

To further demonstrate the versatility of our initiation method presented here, starting groups with electronic functionality were investigated. In this work, we targeted the preparation of initiators carrying an electron-accepting group. Specifically, 4-(5-(9,9-dioctylfluorene)-4-hexyl-2-thienyl)-7-(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole **21** (F8TBT-Br) was employed, since polymer architectures such as F8TBT-P3HT might be useful for photovoltaic applications.[17] In order to test different methods suitable for the preparation of the Grignard precursor at the same time, we employed *tert*-butylmagnesium chloride (^{t}BuMgCl) here. All reaction steps of initiator preparation were carried out in situ in THF-d^8 and monitored via ^{1}H NMR and ^{31}P NMR (see Supporting Information). Thus, Grignard compound **22** was prepared via Grignard metathesis[2] of **21** and ^{t}BuMgCl (Scheme 4). To prepare initiator **23**, an equimolar amount of Ni(dppp)Cl$_2$ was added to the solution of **22**. Figure 3a shows the

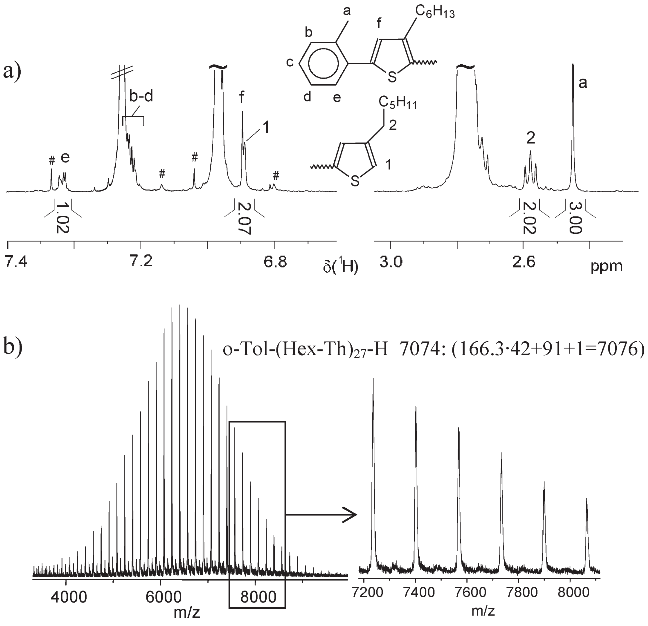
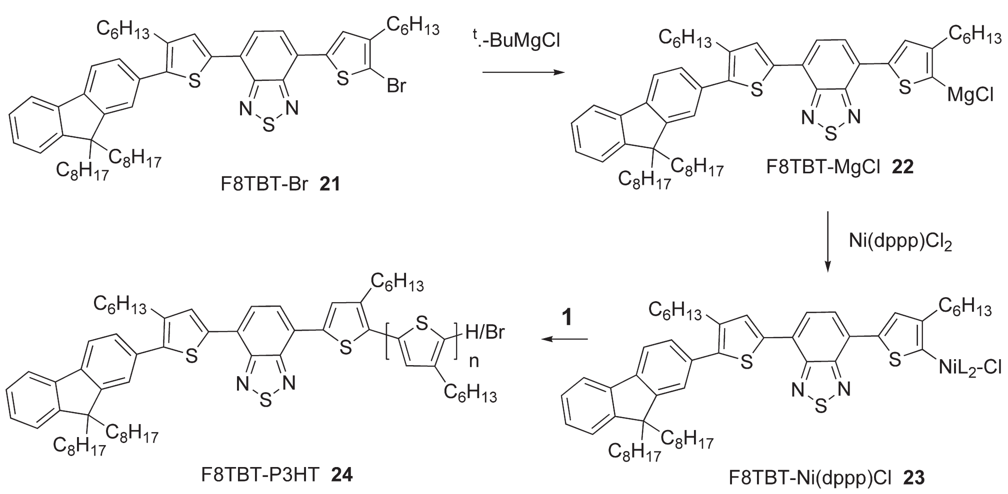


Figure 2. (a) ^{1}H NMR spectrum (regions) of P3HT initiated with monotransmetalation products **16** with assignments of the signals of the starting and end groups. Signals marked with a # are ^{13}C satellites of residual CHCl$_3$ in the solvent CDCl$_3$ and of the aromatic P3HT backbone signal. (b) MALDI-TOF spectrum of the same polymer, showing o-tolyl and hydrogen end groups.

^{31}P NMR spectrum of complex **23**. Clearly, the two doublets of the asymmetric complex are visible, and both chloro as well as bromo adducts were observed. The sharp singlet indicates the formation of Ni(dppp)$_2$, which occurred to a slightly larger extent compared to the simpler tolyl- and thienyl analogues. Polymerization of monomer **1** was initiated by the addition of freshly prepared **23** to the monomer solution, and the reaction mixture was stirred for 30 min. The resulting F8TBT-P3HT **24** was precipitated and purified (see Supporting Information), and investigated by ^{1}H NMR, GPC and MALDI-TOF (see also Supporting Information). The latter technique proved particularly useful to probe the initiation efficiency and the degree of functionalization. Figure 3b shows the MALDI spectrum of **24**. The major peak series corresponds to P3HT with F8TBT as the starting group and hydrogen as end-group, as exemplarily shown for the peak at 3182.7 g/mol ($166.3 \times 14 + 1 + 856.4 = 3185.2$). The second intensive peak series arises from F8TBT/Br end-groups ($166.3 \times 14 + 1 + 856.4 = 3264.5$, peak at 3261.9). We note that only a small fraction of polymer without the F8TBT starting group is observed, namely H/Br terminated P3HT ($166.3 \times 19 + 1 + 79.9 = 3240.6$, peak at 3237.9), which most probably arises from conventional initiation with Ni(dppp)Cl$_2$. Since Br end-groups are found with F8TBT as the starting group, we can also expect Br/Br terminated P3HT, as is demonstrated for the 19-mer ($19 \times 166.3 + 79.9 + 79.9 = 3318.6$, peak at 3317.1). Thus, F8TBT-P3HT **24** exhibits a high degree of F8TBT starting groups, showing that this synthetic approach can easily be extended to more complex heterocyclic initiator precursors. A detailed investigation of the optoelectronic properties of F8TBT-P3HT and the application in organic photovoltaics will be the subject of future investigations.

In conclusion, we have shown that the reactions between NiL$_2$Cl$_2$ and Grignard compounds Ar-MgBr stop after the first transmetalation step, if the aryl groups have alkyl substituent in the *ortho*-position to the bromomagnesium group. As such, this transmetalation reaction is a very convenient and highly selective method for the preparation of initiators for Kumada catalyst-transfer polycondensation reactions from easily available compounds.[18] This developed

Scheme 4. Preparation of Ni Initiators with Electronic Functionality from Ni(dppp)Cl_2 and Sterically Hindered Grignard F8TBT-MgCl 22 Followed by Polymerization of 1



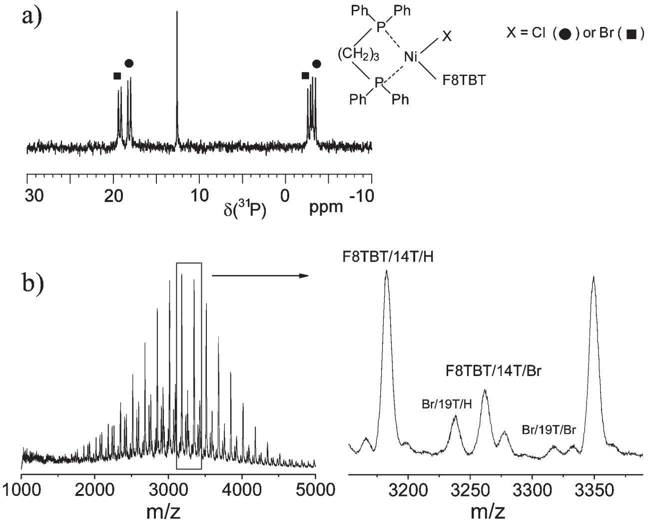


Figure 3. (a) ^{31}P NMR of complex F8TBT-NidpppBr/Cl (**23**). The sharp singlet arises from the formation of Ni(dppp)$_2$. (b) Complete MALDI-ToF spectrum of F8TBT-P3HT (**24**) (left) and section showing the different peak series with F8TBT/H, F8TBT/Br, Br/Br and H/Br terminated P3HT chains (right).

method allows the initiation of KCTP, and the polymerization of 2-bromo-5-chloromagnesio-3-hexylthiophene results in the corresponding aryl-terminated poly(3-hexylthiophene)s with high initiation efficiencies. Since the initiation of more complex heterocycles with electronic functionality proceeds with high yield as well, we envisage further extensions and applications in the field of multifunctional conjugated polymer architectures.

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Supporting Information Available: Text giving experimental details and characterization and figures showing NMR spectra and GPC curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) ^{31}P NMR data at 0 °C in THF-d$_8$ (δ; J_{PP}): **16-dppe**, 53.0 and 35.3 ppm, 17 Hz; **16-dppe-Br**, 55.5 and 35.5 ppm, 18 Hz; **20-dppe**, 55.1 and 38.5 ppm, 35 Hz; **20-dppe-Br**, 58.4 and 42.8 ppm, 34 Hz; **16-dppp**, 20.7 and −4.8 ppm, 44 Hz; **16-dppp-Br**, 21.1 and −4.6 ppm, 44 Hz; **20-dppp**, 17.9 and −4.2 ppm, 63 Hz; **20-dppp-Br**, 19.0 and −3.6 ppm, 63 Hz.

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