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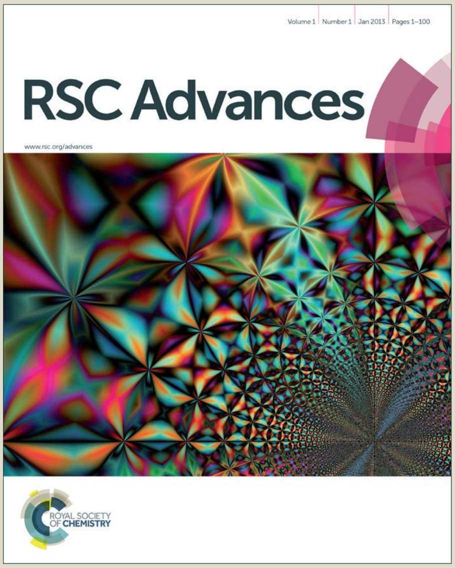

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ARTICLE

Highly α-Regioselective Neodymium-Mediated Allylation of Diaryl Ketones

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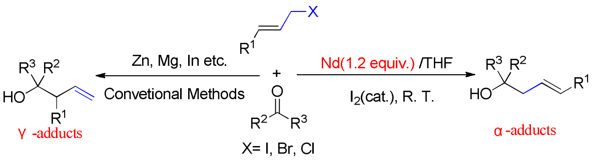
The first utility of neodymium as a mediating-metal in the highly α-regioselective Barbier reaction of diaryl ketones with allyl halides was reported in this paper. This reaction was conveniently carried out under mild conditions in a one-pot fashion with moderate to good yields. The protocol constituted an availability of starting material, wide substrate scope, operational simplicity and powerful alternative approach.

Introduction

Since pioneering studies by Kagan and co-workers demonstrated the particular effectiveness of samarium (Ⅱ) diiodide as a strong one-electron transfer reducing agent,[1] the utilization of SmI_2 reagent in synthetic organic chemistry has been dramatically documented.[2] Then, some “new” soluble divalent lanthanide reagents, LnX_2 (Ln = Nd,[3] Dy,[4] Tm,[5] X = I, Br, Cl) have been reported. Compared with SmI_2 [6], NdX_2 has a Ln(III)/Ln(II) reduction potential vs NHE of -2.6 V which was much smaller. And the first utility of NdI_2 as a reductant was reported by Evans.[3] In their research, alkyl halides reacted with ketone or aldehyde in the presence of 2.2 equiv. neodymium(II) diiodide. The elegant result indicated that the NdI_2 can be a single electron transfer reagent which is similar to SmI_2. However, NdI_2 is moisture- and air-sensitive, which is instable in solvent at room temperature. And the preparation is much more difficult than SmI_2. For above reasons, the application of NdI_2 in organic chemistry is still scarcely reported.

As known to us, the zerovalent lanthanoid metals could also bear strong reduction potential.[7] In particular, Ce,[8] Sm,[9] Dy,[10] Yb[11] and La[12] have been employed as useful reagents or catalysts in organic synthesis. They show great advantages not only nontoxic and cheap, but also stability in the air. However, never a successful application of reduction of zerovalent neodymium metal has been reported. More recently, our group have been deeply interested in lanthanide reagents[13] and wanted to explore new application of lanthanide metals in organic synthesis. Inspired by Evans's research, the reaction of allyl halides and carbonyl compounds mediated by neodymium metal was investigated in this paper.

In principle, the metal-mediated allylation of carbonyl compounds is one of the reliable methods to construct homoallylic alcohols. However, most of these metal-mediated or –catalyzed reactions are γ-selective to give γ-adducts.[14] And α-adducts of crotyl bromide and prenyl bromide with aldehyde or ketone play an important role in organic synthesis.[15] Many endeavor has been made to realized α-selective allylation of carbonyl compounds. Yamamoto's group reported the first alpha-regioselective allylation of allylbarium reagents. They first direct preparation of allylbarium reagents by reaction of in situ generated reactive barium with various allylic chlorides and their new and unexpected selective allylation reactions with carbonyl compounds are disclosed. Loh's group subsequently reported α-selective crotylation of aldehyde which was medated by indium or tin[16] (Scheme 1). Wang's group realized the regioselective allylation of aldehyde by the use of $NaBF_4$ and metal.[17] And the α-selective allylation of ketone was first reported by Zhao and co-workers.[18] Due to high temperature lead to increase of α-addition products, high boiling solvents were essential in their research. In this paper, a neodymium-mediated α-selective allylation of ketone and easter was developed without any other additves. This strategy provided a broad scope and moderate to good yields of the α-addition products.



Scheme 1. Regioselective of metal-mediated Barbier reaction

Results and discussion

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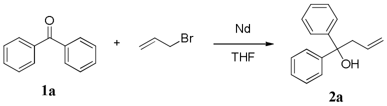
When benzophenone (**1a**) was treated with allyl bromide and Nd in THF under a nitrogen atmosphere at room temperature, 1,1-diphenylbut-3-en-1-ol (**2a**) were obtained (Scheme 2).



Scheme 2. One-pot reaction of benzophenone in the presence of neodymium metal

Encouraged by this reaction, we selected it as a model reaction for optimizing reaction conditions. A systematic study was carried out for evaluating the molar ratio of Nd and allyl bromide, temperature and the solvent. The results were summarized in Table 1. The use of 1.2 equiv. of neodymium and 1.5 equiv. of allyl bromide was found to be optimal (Table 1, entries 1-5). Furthermore, the reaction efficiency was found to be affected by the solvent system, solvent had a marked influence on the product formation, when the reaction was performed at room temperature in DME, toluene, MTBE, diethyl ether or H_2O instead of THF as the solvent, no product was obtained (Table 1, entries 6-10). In regard to the influence of temperature on the reaction, it was found that the yield of **2a** decreased to 50% at -20 ^{o}C (Table 1, entries 11-12). Thus, product **2a** could be obtained in excellent yield when the reaction was conducted at room temperature and THF as the solvent with a 1.5/1.2/1 molar ratio of halide, neodymium and **1a**.

With the above optimized reaction conditions (1.2 equiv. of neodymium and 1.5 equiv. of halide at 25 ^{o}C in THF) in hand, the reactions of a variety of bromide with ketone were subsequently explored and the results were summarized in Table 2. As shown in Table 2, when allyl bromide was treated with various ketones, good yields were obtained with aromatic ketones bearing electron-donating on the aryl ring, such as 4-methyl-, 4- phenyl-, 4,4'-dimethoxy-benzophenone (Table 2, entries 2-5). With aromatic ketones bearing electron-withdrawing groups on the aryl ring, such as 4-fluoro-, 4-chloro-, and 3,4-dichloro-benzophenone, the products were obtained in moderate yields (Table 2, entries 6-8). The above results showed that electron-donating groups on the aryl ring were more favorable for the reaction than electron-withdrawing groups. To our dismay, the reactions with benzaldehyde, an unsaturated aldehyde, 1-phenylbutan-1-one and (*E*)-chalcone with allyl bromide were messy and no titled products were obtained. (Table 2, entries 9-12).

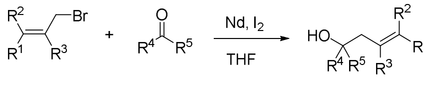
To study the regioselectivity of this allylation, 3,3-dimethylallyl bromide, cinnamyl bromide and crotyl bromide were tested. To our delight, the reactions could also proceed smoothly and afford corresponding α-addition alcohols exclusively in good yields (Table 2, entries 13-23). When the secondary alkyl halide was treated with benzophenone, and methallyl halide with benzophenone, phenyl(p-tolyl)methanone and bis(4-chlorophenyl)methanone, no title products were obtained (Table 2, entries 24-27).

Table 1. Optimization of Reaction Conditions^{a}

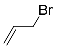
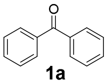
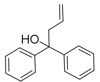
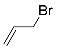
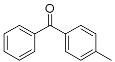
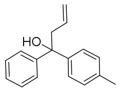
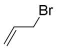
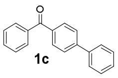
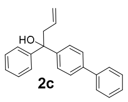
Entry	Ratio^{b}	Solvent	Temp (^{o}C)	Yield (%)^{c}
1	6:2:1	THF	25	75
2	4:2:1	THF	25	78
3	2:2:1	THF	25	76
4	1.5:1.2:1	THF	25	84
5	1.5:0.6:1	THF	25	53
6	1.5:1.2:1	DMF	25	None
7	1.5:1.2:1	toluene	25	None
8	1.5:1.2:1	MTBE	25	None
9	1.5:1.2:1	Et_2O	25	None
10	1.5:1.2:1	H_2O	25	None
11	1.5:1.2:1	THF	0	67
12	1.5:1.2:1	THF	-20	50

[a] To a suspension of benzophenone (0.5 mmol) and neodymium in THF (3 mL) was added allylicbromide and catalytic amounts of I_2 under a nitrogen atmosphere at room temperature, and the mixture was stirred for 2h. [b] Ratio = allylbromide:metal:benzophenone [c] Isolated yield based on benzophenone after silica gel chromatography.

Table 2. One-pot reaction of ketones and bromides in the presence of neodymium metal and catalytic amounts of iodine in THF^{a}



1a-m
2a-2a'

Entry	Bromide	Substrate	Product	Yield (%)^{b}
1		 **1a**	 **2a**	84
2		 **1b**	 **2b**	80
3		 **1c**	 **2c**	94

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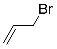
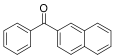
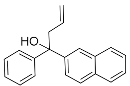
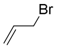
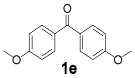
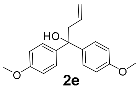
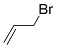
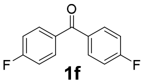
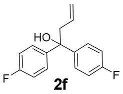
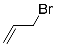
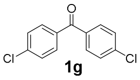
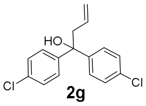
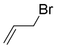
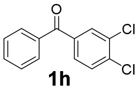
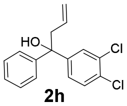
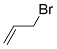
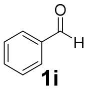
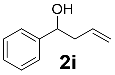
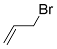
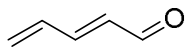
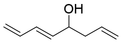
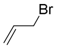
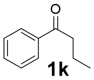
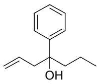
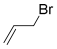
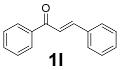
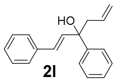
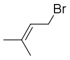
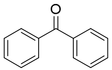
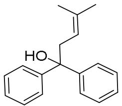
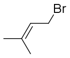
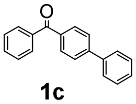
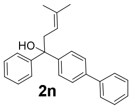
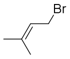
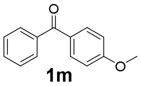
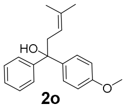
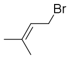
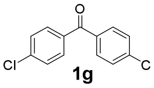
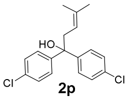
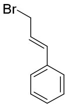
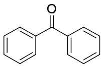
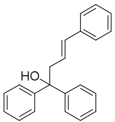
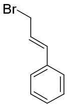
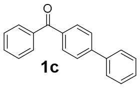
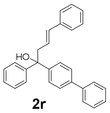
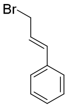
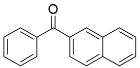
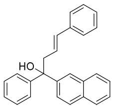
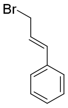
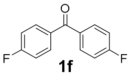
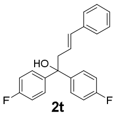
4		 **1d**	 **2d**	92
5		 **1e**	 **2e**	88
6		 **1f**	 **2f**	77
7		 **1g**	 **2g**	75
8		 **1h**	 **2h**	71
9		 **1i**	 **2i**	0
10		 **1j**	 **2j**	0
11		 **1k**	 **2k**	0
12		 **1l**	 **2l**	0
13		 **1a**	 **2m**	88
14		 **1c**	 **2n**	85
15		 **1m**	 **2o**	78
16		 **1g**	 **2p**	75
17		 **1a**	 **2q**	80
18		 **1c**	 **2r**	66
19		 **1d**	 **2s**	75
20		 **1f**	 **2t**	77

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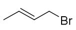
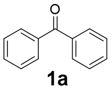
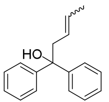
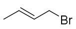
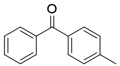
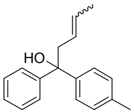
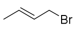
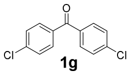
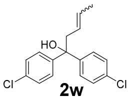
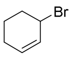
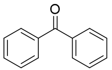
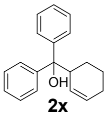
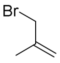
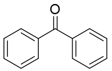
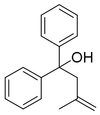
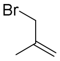
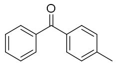
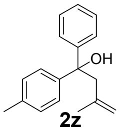
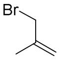
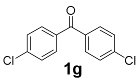
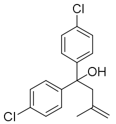
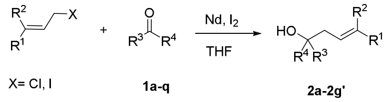
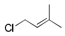
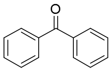
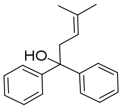
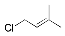
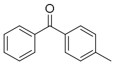
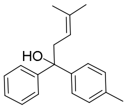
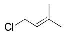
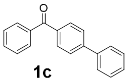
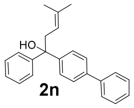
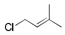
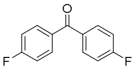
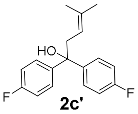
21		 **1a**	 **2u**	77
22		 **1b**	 **2v**	70
23		 **1g**	 **2w**	69
24		 **1a**	 **2x**	0
25		 **1a**	 **2y**	0
26		 **1b**	 **2z**	0
27		 **1g**	 **2a'**	0

[a] To a suspension of carbonyl compounds (0.5 mmol) and neodymium (0.6 mmol) in THF (3 mL) was added bromide (0.75 mmol) and catalytic amounts of I_2 under a nitrogen atmosphere, and the mixture was stirred for 2 h. [b] Isolated yield based on the substrates after silica gel chromatography.

Experiments to further explore the scope of halides were then conducted, 3,3-dimethylallyl chloride and allyl iodide were subjected to this reaction and the results were summarized in Table 3. As we can see, when 3,3-dimethylallyl chloride was applied with various ketones, it could undergo reaction smoothly to afford the desired α-adducts with moderate to good yields (Table 3, entries 1-6). Then, we turned our attention to the reaction of allyl iodide with ketones 1a, 1c, 1d and 1e. Fortunately, they showed quite good performance giving the desired products in excellent yields (Table 3, entries 7-10). 9-Fluorenone 1n could also be well tolerated and the product was obtained in good yield (Table 3, entry 11). Heterocyclic ketones 1o-1p could also react with allyl iodide providing the products 2e'-2f' in moderate yields (Table 3, entries 12-13). Then, we were pleased to find that the reaction was successfully extended to acetophenone with a moderate yield (Table 3, entry 14).

Table 3. One-pot reaction of ketones and halides in the presence of neodymium metal and catalytic amounts of iodine in THF[a]



Entry	Halide	Substrate	Product	Yield (%)[b]
1		 **1a**	 **2m**	70
2		 **1b**	 **2b'**	55
3		 **1c**	 **2n**	93
4		 **1f**	 **2c'**	50

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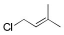
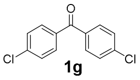
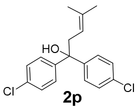
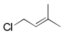
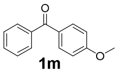
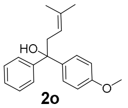
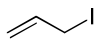
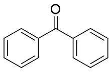
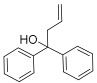
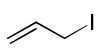
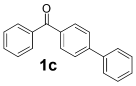
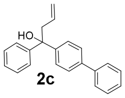
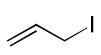
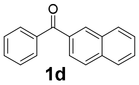
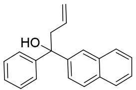
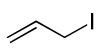
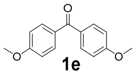
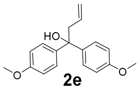
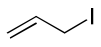
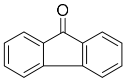
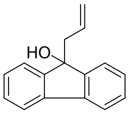
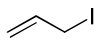
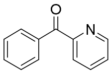
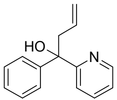
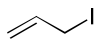
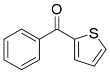
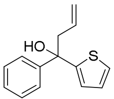
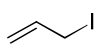
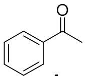
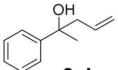
5		 1g	 2p	70
6		 1m	 2o	75
7		 1a	 2a	90
8		 1c	 2c	90
9		 1d	 2d	94
10		 1e	 2e	88
11		 1n	 2d'	70
12		 1o	 2e'	50
13		 1p	 2f'	65
14		 1q	 2g'	55

[a] To a suspension of carbonyl compounds (0.5 mmol) and neodymium （0.6 mmol） in THF (3 mL) was added halide (0.75 mmol) and catalytic amounts of I_2 under a nitrogen atmosphere, and the mixture was stirred for 2 h. [b] Isolated yield based on the substrates after silica gel chromatography.

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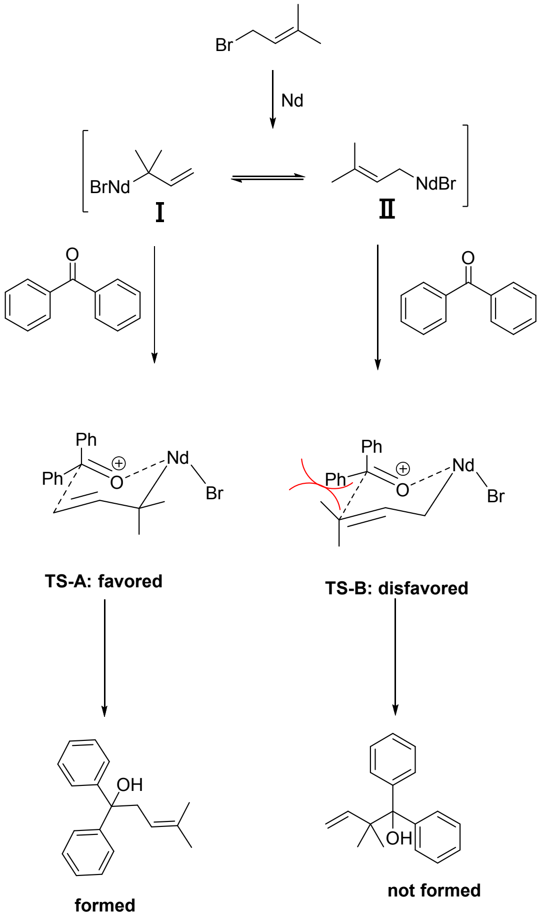
Although a detailed mechanism requires further investigation, a plausible reaction mechanism was proposed in Scheme 3. Firstly, the allyl neodymium reagents were generated in situ by the reaction of neodymium and allyl halides. The allyl neodymium reagents interconverted between primary allyl species I and tertiary allyl species II.[19] Consequently, there were two possible pathways for the reaction of allyl neodymium reagents with ketones. Of the two possible transition states A and B, TS-A would be more favorable because of the absence of steric interactions between the phenyl group and the methyl group of the terminal olefin, which was presence in TS-B. Consequently, the TS-A thus formed would undergo the addition reaction to give the α-addition products with highly regioselectivity.



Scheme 3. plausible reaction mechanism

Experimental

General Methods. THF was distilled from sodium benzophenone under nitrogen. All reactions were conducted under a nitrogen atmosphere. Metallic neodymium and all solvents were purchased from commercial source, without further purification before use. The flash column chromatography was carried out on Merck silica gel (300–400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Varian-Inova-400 spectrometer. Solvent for NMR is $CDCl_3$, unless the otherwise noted. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on 100 MHz. Chemical shifts are reported in parts per million relatived to the central line of the multiplet at 77.5 ppm for $CDCl_3$. High-resolution mass spectra were obtained with a GCT-TOF instrument. All chemicals were purchased from Aldrich, Alfa or Acros chemical company and used thus, without further purification. Petroleum ether (PE) used refers to the 60–90^{o}C boiling point fraction of petroleum.

General procedure for synthesis of alcohol(2a-2g').

To a suspension of carbonyl compounds (0.5 mmol) and neodymium（0.6 mmol）in THF (3 mL) was added halide (0.75 mmol) and catalytic amounts of I_2 under a nitrogen atmosphere at room temperature. The mixture was stirred for 2 h and then was quenched with dilute hydrochloric acid. The resulting mixture was extracted with diethyl ether (3×10 mL), and dried over anhydydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure. Purification by column chromatography on silica gel afforded olefins (300–400 mesh, petroleum ether as eluent).

1,1-diphenylbut-3-en-1-ol (2a).[20]

The title compound was obtained according to the general procedure. Yellow oil: 101 mg，90%; IR (KBr): 3555, 3056, 2919, 2843, 1944, 1770, 1641, 1560, 1469, 1386, 1168, 992, 810, 765, 698cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.37-7.15 (m, 10H), 5.61-5.53 (m, 1H), 5.17-5.07 (m, 2H), 2.96 (d, J = 7.06 Hz, 2H), 2.49 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 146.90, 133.86, 128.63, 127.32, 126.41, 121.02, 77.30, 47.12. HRMS (ESI) m/z (M+Na+) calcd for C16H16O, 224.1202, found: 224.1203.

1-phenyl-1-p-tolylbut-3-en-1-ol (2b).

The title compound was obtained according to the general procedure. Yellow oil: 95 mg, 80%; IR (KBr): 3557, 3063, 3025, 2972, 2921, 1950, 1639, 1511, 1445, 1383, 991, 815, 763, 699cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.34 (d, J = 7.6 Hz, 2H), 7.24-7.18 (m, 4H), 7.12-7.09 (m, 1H), 7.02 (d, J = 7.6 Hz, 2H), 5.62-5.52 (m, 1H), 5.15-5.05 (m, 2H), 2.96 (d, J = 7.1 Hz, 2H), 2.44 (s, 1H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 147.13, 144.07, 136.88, 134.01, 129.32, 128.58, 127.21, 126.52, 126.37, 120.77, 77.23, 47.16, 21.42. HRMS (ESI) m/z (M+H+) calcd for $C_{17}H_{18}O$: 238.1358; found: 238.1354.

1-phenyl-1-(4'-phenyl)phenylbut-3-en-1-ol(2c).[21]

The title compound was obtained according to the general procedure. Yellow oil: 141 mg, 94%; IR (KBr): 3550, 3070, 2919, 2836, 1950, 1773, 1626, 1516, 1458, 1385, 1174, 929, 810, 766, 686cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.45-7.35 (m, 8H), 7.27 (d, J = 7.2 Hz, 2H), 7.21-7.18 (m, 3H), 7.11-7.08 (m, 1H), 5.60-5.54 (m, 1H), 5.14-5.04 (m, 2H), 2.97 (d, J = 7.1 Hz, 2H), 2.50 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 146.84, 146.01, 141.09, 140.06, 133.81, 129.16, 128.66, 127.66, 127.45, 127.34, 127.32, 126.87,

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126.40, 121.00, 77.18, 47.11. HRMS (ESI) m/z (M+H+) calcd for $C_{22}H_{20}O$: 300.1514; found: 300.1514.

1-(naphthalen-3-yl)-1-phenylbut-3-en-1-ol (2d).

The title compound was obtained according to the general procedure. Yellow oil: 252 mg, 92%; IR (KBr): 3538, 3046, 2912, 2844, 1905, 1765, 1629, 1516, 1468, 1386, 1107, 929, 822, 736, 659cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.88 (s, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.68-7.64 (m, 2H), 7.39-7.33 (m, 5H), 7.20 (t, J = 7.2 Hz, 2H), 7.13-7.09 (m, 1H), 5.18-5.13 (m, 1H), 5.08-5.05 (m, 2H), 3.09-3.05 (m, 2H), 2.58(s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 146.74, 144.24, 133.81, 133.46, 132.76, 127.93, 124.60, 121.03, 77.82, 77.50, 46.92. HRMS (ESI) m/z (M+H+) calcd for: 274.1358, found: 274.1356.

1,1-bis(4-methoxyphenyl)but-3-en-1-ol (2e).[22]

The title compound was obtained according to the general procedure. Yellow oil: 125 mg, 88%; IR (KBr): 3499, 3073, 2934, 2835, 2546, 2049, 1893, 1610, 1513, 1463, 1385, 991, 828, 736cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.25 (d, J = 8.4 Hz, 2H), 6.74 (d, J = 8.4 Hz, 2H), 5.63-5.53 (m, 1H), 5.14-5.05 (m, 2H), 3.67(s, 6H), 2.92 (d, J = 6.9 Hz, 2H), 2.44 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 158.72, 139.46, 134.21, 134.10, 127.89, 127.39, 120.54, 114.01, 113.61, 76.86, 55.73, 55.49, 47.38. HRMS (ESI) m/z (M+H+) calcd for $C_{18}H_{20}O_3$: 284.1412, found: 284.1410.

1,1-bis(4-fluorophenyl)but-3-en-1-ol (2f). [22]

The title compound was obtained according to the general procedure. Yellow oil: 100 mg, 77%; IR (KBr): 3554, 3086, 2912, 2844, 1956, 1726, 1637, 1560, 1486, 1356, 1107, 987, 820, 769, 689cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.29 (dd, J =14.0 Hz, J = 3.1 Hz, 4H), 6.90 (t, J = 8.6 Hz, 4H), 5.57-5.50 (m, 1H), 5.17-5.09 (m, 2H), 2.93 (d, J = 7.18 Hz, 2H), 2.50 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.41, 161.00, 160.99, 160.96, 142.60, 133.40, 133.31, 128.46, 128.38, 127.95, 127.88, 121.50, 121.46, 115.78, 115.57, 115.34, 115.13, 76.71, 47.32. HRMS (ESI) m/z (M+H+) calcd for $C_{16}H_{14}F_2O$: 260.1013, found: 260.1010.

1,1-bis(4-chlorophenyl)but-3-en-1-ol (2g). [23]

The title compound was obtained according to the general procedure. Yellow oil: 110 mg, 75%; IR (KBr): 3550, 3080, 2977, 2850, 1907, 1776, 1639, 1593, 1490, 1400, 1093, 927, 820, 756, 671cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.23 (d, J = 8.4 Hz, 4H), 7.16 (d, J = 8.4 Hz, 4H), 5.51-5.49 (m, 1H), 5.14-5.07 (m, 2H), 2.89 (d, J = 7.2 Hz, 2H), 2.51(s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 145.02, 133.35, 133.00, 128.82, 127.82, 121.64, 76.65, 46.88. HRMS (ESI) m/z (M+H+) calcd for $C_{16}H_{14}Cl_2O$: 294.0392; found: 294.0393.

1-(3,4-dichlorophenyl)-1-phenylbut-3-en-1-ol (2h).[24]

The title compound was obtained according to the general procedure. Yellow oil: 104 mg, 71%; IR (KBr): 3545, 3068, 2921, 2844, 1950, 1762, 1637, 1561, 1468, 1382, 1170, 992, 822, 766, 699cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.49 (s, 1H), 7.32 (d, J = 7.2 Hz, 2H), 7.25-7.21 (m, 3H), 7.16-7.12 (m, 2H), 5.54-5.50 (m, 1H), 5.16-5.09 (m, 2H), 2.99-2.85 (m, 2H), 2.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 147.35, 145.83, 132.73, 130.58, 128.90, 127.81, 125.97, 121.69, 77.82, 77.50, 77.18, 76.69, 46.83. HRMS (ESI) m/z (M+H+) calcd for $C_{16}H_{14}Cl_2O$: 292.0422;

4-methyl-1,1-diphenylpent-3-en-1-ol (2m).[22]

The title compound was obtained according to the general procedure. Yellow oil: 144 mg, 88%; IR (KBr): 3545, 3085, 3029, 2921, 1950, 1663, 1600, 1446, 1381, 1260, 1167, 1054, 905, 754, 700, 642cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.37-7.09 (m, 10H), 4.96 (t, J = 7.2 Hz, 1H), 2.92 (d, J = 7.3 Hz, 2H), 2.47 (s, 1H), 1.58 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 147.41, 138.31, 128.55, 127.15, 126.49, 118.89, 78.10, 77.82, 77.50, 77.18, 41.27, 26.56, 18.74. HRMS (ESI) m/z (M+H+) calcd for $C_{18}H_{20}O$: 252.1514, found: 252.1512.

4-methyl-1-phenyl-1-(4'-phenyl)phenylpent-3-en-1-ol (2n).

The title compound was obtained according to the general procedure. Yellow oil: 117 mg, 93%; IR (KBr): 3550, 3058, 3045, 2912, 1955, 1668, 1601, 1464, 1381, 1255, 1168, 1056, 906, 745, 700, 645cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.47-7.39 (m, 8H), 7.30 (t, J = 7.6 Hz, 2H), 7.24-7.20 (m, 3H), 7.14-7.08 (m, 1H), 4.98 (s, 1H), 2.95 (d, J = 7.1 Hz, 2H), 2.51 (s, 1H), 1.59(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 147.30, 146.48, 141.21, 139.93, 138.48, 128.61, 127.47, 127.21, 126.46, 118.82, 77.99, 77.82, 77.50, 77.18, 41.27, 26.59, 18.79. HRMS (ESI) m/z (M+H+) calcd for $C_{24}H_{24}O$: 328.1827, found: 2328.1829.

1-(4-methoxyphenyl)-4-methyl-1-phenylpent-3-en-1-ol (2o).

The title compound was obtained according to the general procedure. Yellow oil: 110 mg, 78%; IR (KBr): 3517, 3029, 2912, 2833, 2041, 1887, 1765, 1610, 1510, 1445, 1383, 1248, 1178, 902, 828, 763, 701cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.42 (d, J = 7.6 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.20-7.17 (m, 1H), 6.82 (d, J = 8.8 Hz, 2H), 5.06-5.03 (m, 1H), 3.74 (s, 3H), 2.97 (d, J = 7.2 Hz, 2H), 2.53 (s, 1H), 1.66 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 158.71, 147.79, 139.68, 137.96, 128.47, 127.02, 126.42, 119.06, 113.83, 77.87, 77.82, 77.50, 77.18, 55.59, 41.39, 26.52, 18.71. HRMS (ESI) m/z (M+H+) calcd for $C_{19}H_{22}O_2$: 282.1620, found: 282.1618.

1,1-bis(4-chlorophenyl)-4-methylpent-3-en-1-ol (2p).

The title compound was obtained according to the general procedure. Yellow oil: 120 mg, 75%; IR (KBr): 3540, 3026, 1896, 1762, 1600, 1447, 1405, 1380, 1156, 971, 832, 748, 696cm^{-1};^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 7.27-7.24 (m, 4H), 7.18-7.16 (m, 4H), 4.90 (t, J = 6.8 Hz, 1H), 2.85 (d, J = 7.2 Hz, 2H), 2.48 (s, 1H), 1.59-1.57 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.51, 139.18, 133.24, 128.78, 127.90, 118.08, 77.45, 41.09, 26.57, 18.75. HRMS (ESI) m/z (M+H+) calcd for $C_{18}H_{18}Cl_2O$: 320.0735, found: 320.0733.

(E)-1,1,4-triphenylbut-3-en-1-ol (2q).[25]

The title compound was obtained according to the general procedure. Yellow solid: 120 mg, 80%; mp 82-83.4 °C. IR (KBr): 3537, 3080, 2884, 1955, 1751, 1595, 1491, 1353, 1199, 968, 867, 776, 694cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.53-7.51 (m, 4H), 7.39-7.35 (m, 3H), 7.30-7.24 (m, 7H), 6.61 (d, J = 15.8 Hz, 1H), 6.11-6.07 (m, 1H), 3.26 (d, J = 7.3 Hz, 2H), 2.64 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 147.00, 137.33, 135.77, 128.94, 128.67, 127.95, 127.37, 126.70, 126.47, 125.06, 77.83, 77.50, 77.18, 46.46. HRMS (ESI) m/z (M+H+) calcd for $C_{22}H_{20}O$: 300.1514, found: 300.1517.

(E)-1-([1,1'-biphenyl]-4-yl)-1,4-diphenylbut-3-en-1-ol (2r).

The title compound was obtained according to the general procedure. Yellow solid: 141 mg, 75%; mp 73-74.8 °C. IR (KBr): 3540, 3025, 2830, 1944, 1796, 1603, 1486, 1342, 1064, 968, 841, 695cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.46-7.05 (m, 19H), 6.44 (d, J = 15.9 Hz, 1H), 5.98-5.94 (m, 1H), 3.11 (d, J = 7.2 Hz, 2H), 2.53 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS):146.91, 146.08, 140.10, 135.84, 129.18, 128.72, 127.96, 127.69, 127.47, 127.42, 127.36,

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126.92, 126.71, 126.45, 124.97, 77.82, 77.72, 77.50, 77.18, 46.47. HRMS (ESI) m/z (M+H+) calcd for $C_{28}H_{24}O$: 376.1827, found: 376.1826.

(E)-1-(naphthalen-3-yl)-1,4-diphenylbut-3-en-1-ol (2s).

The title compound was obtained according to the general procedure. Yellow solid: 135 mg, 77%; mp 93-94.5 °C. IR (KBr): 3528, 3020, 2830, 1950, 1779, 1600, 1491, 1359, 1121, 967, 826, 746, 697cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.99 (s, 1H), 7.83-7.74 (m, 3H), 7.51-7.43 (m, 5H), 7.32-7.15 (m, 8H), 6.57 (d, J = 15.9 Hz, 1H), 6.08-6.04(m, 1H), 3.30-2.28 (m, 2H), 2.71 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 146.81, 144.34, 137.27, 135.94, 133.52, 132.83, 128.95, 128.77, 128.73, 128.49, 127.99, 127.96, 127.50, 126.73, 126.58, 126.56, 126.41, 125.32, 124.94, 124.68, 77.95, 46.32. HRMS (ESI) m/z (M+H+) calcd for $C_{26}H_{22}O$: 350.1671, found: 350.1670.

(E)-1,1-bis(4-fluorophenyl)-4-phenylbut-3-en-1-ol (2t).

The title compound was obtained according to the general procedure. Yellow oil: 111 mg, 66%; IR (KBr): 3545, 3085, 2875, 1945, 1740, 1585, 1490, 1335, 1199, 978, 865, 776, 695cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.33-7.30 (m, 4H), 7.18-7.11 (m, 5H), 6.94-6.89 (m, 4H), 6.46 (d, J = 15.9 Hz, 1H), 5.94-5.86 (m, 1H), 3.06 (d, J = 7.3 Hz, 2H), 2.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.43, 160.98, 142.66, 142.64, 137.11, 136.14, 128.24, 128.16, 126.7, 124.37, 115.59, 115.38, 77.81, 77.50, 77.21, 77.19, 46.62. HRMS (ESI) m/z (M+H+) calcd for $C_{22}H_{18}F_2O$: 336.1326, found: 336.1325.

1,1-diphenylpent-3-en-1-ol (2u) [26] **(E/Z = 4:1)**

The title compound was obtained according to the general procedure. Yellow oil: 92 mg, 77%; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.48-7.17 (m, 10H), 5.71-5.23 (m,2H), 3.07＆2.98 (m, J = 8 Hz, 2H), 2.63-2.53 m, 1H), 1.66-1.61 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 146.70, 131.80, 129.30, 128.06, 126.74, 126.67, 125.95, 125.46, 124.59, 77.58, 76.68, 45.52, 39.46, 18.10, 13.19. HRMS (ESI) m/z (M+H+) calcd for $C_{17}H_{18}O$: 238.1358, found: 238.1356.

1-phenyl-1-(p-tolyl)pent-3-en-1-ol (2v) (E/Z = 3.3:1)

The title compound was obtained according to the general procedure. Yellow oil: 88 mg, 70%;^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.45-7.09 (m, 9H), 5.67-5.29 (m,2H), 3.05＆2.98 (m, J = 8 Hz, 2H), 2.59-2.49 m, 1H), 1.66-1.61 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 146.91, 143. 82, 136.31, 136.22, 131.65, 129.13, 128.76, 128.02, 126.64, 126.57, 125.90, 125.59, 124.73, 77.49, 76.66, 45.55, 39.50, 20.91, 18.10, 13.19. HRMS (ESI) m/z (M+H+) calcd for $C_{18}H_{20}O$: 252.1514, found: 252.1513.

1,1-bis(4-chlorophenyl)pent-3-en-1-ol (2w) (E/Z = 4:1)

The title compound was obtained according to the general procedure. Yellow oil: 112 mg, 69%; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.46-7.23 (m, 8H), 5.74-5.18 (m,2H), 3.00＆2.915 (m, J = 8 Hz＆J = 4 Hz, 2H), 2.64-2.53 m, 1H), 1.65-1.60 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 144.82, 132.85, 132.78, 132.64, 130.15, 128.31, 127.38, 124.66, 123.73, 76.12, 45.33, 39.29, 18.13, 13.22. HRMS (ESI) m/z (M+H+) calcd for $C_{17}H_{16}Cl_2O$: 306.0578, found: 306.0579.

4-methyl-1-phenyl-1-(p-tolyl)pent-3-en-1-ol (2b').

The title compound was obtained according to the general procedure. Yellow oil: 67 mg, 50%; IR (KBr): 3545, 3023, 2920, 1941, 1802, 1674, 1600, 1511, 1446, 1383, 1167, 1058, 1001, 879, 814, 761, 701, 642cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.45-7.42 (m, 2H), 7.34-7.27 (m, 4H), 7.11 (d, J = 8.0 Hz, 2H), 5.07-5.03 (m, 1H), 2.99 (d, J = 7.2 Hz, 2H), 2.51 (s, 1H), 2.30 (s, 3H), 1.67 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 147.62, 144.54, 138.18, 136.72, 129.27, 128.52, 127.06, 126.44, 119.02, 78.00, 41.30, 26.56, 21.44, 18.76. HRMS (ESI) m/z (M+H+) calcd for $C_{19}H_{22}O$: 266.1671, found: 266.1670.

1,1-bis(4-fluorophenyl)-4-methylpent-3-en-1-ol (2c').

The title compound was obtained according to the general procedure. Yellow oil: 79 mg, 55%; IR (KBr): 3531, 3054, 2980, 1896, 1660, 1602, 1506, 1443, 1383, 1227, 1160, 1067, 912, 833, 734, 669cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.41-7.36 (m, 4H), 7.01-6.91 (m, 4H), 5.02-4.98 (m, 1H), 2.96 (d, J = 7.6 Hz, 2H), 2.56 (s, 1H). 1.68 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 163.36, 160.92, 143.07, 143.04, 138.85, 128.25, 128.17, 118.39, 115.46, 115.25, 77.52, 41.47, 26.55, 18.72. HRMS (ESI) m/z (M+H+) calcd for $C_{18}H_{18}F_2O$: 288.1326, found: 288.1327.

9-allyl-9H-fluoren-9-ol (2d'). [26]

The title compound was obtained according to the general procedure. Yellow oil: 78 mg, 70%; IR (KBr): 3301, 3068, 2929, 1879, 1640, 1583, 1448, 1388, 1197, 1054, 915, 761, 735, 672cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.56 (d, J = 7.6 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H), 7.33-7.22 (m, 4H), 5.57-5.46 (m, 1H), 4.92-4.88 (m, 2H), 2.76 (d, J = 7.2 Hz, 2H), 2.31 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 148.70, 139.80, 133.10, 129.34, 128.23, 124.31, 120.33, 119.15, 81.95, 44.45. HRMS (ESI) m/z (M+H+) calcd for $C_{16}H_{14}O$: 222.1045, found: 222.1047.

1-phenyl-1-(pyridin-2-yl)but-3-en-1-ol (2e').

The title compound was obtained according to the general procedure. Yellow oil: 56 mg, 50%; IR (KBr): 3540, 3060, 2364, 1958, 1745, 1639, 1590, 1493, 1445, 1384, 916, 752, 700cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 8.51 (d, J = 4.4 Hz, 1H), 7.65-7.61 (m, 1H), 7.55-7.53 (m, 2H), 7.37-7.29 (m, 3H), 7.25-7.19 (m, 1H), 7.17-7.13 (m, 1H), 5.78-5.68 (m, 1H), 5.57 (s, 1H), 5.12-5.02 (m, 2H), 3.15-3.04 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 163.69, 147.86, 146.38, 137.35, 134.08, 128.67, 127.42, 126.46, 122.48, 121.21, 119.06, 77.33, 46.19. HRMS (ESI) m/z (M+H+) calcd for $C_{15}H_{15}NO$: 225.1154, found: 225.1155.

1-phenyl-1-(thiophen-2-yl)but-3-en-1-ol (2f').

The title compound was obtained according to the general procedure. Yellow oil:75 mg, 65%; IR (KBr): 3537, 3071, 2921, 2835, 1955, 1893, 1723, 1638, 1600, 1493, 1445, 1384, 1232, 1036, 986, 919, 828, 764, 699cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.51-7.49 (m, 2H), 7.33 (t, J = 7.2 Hz, 2H), 7.26-7.19 (m, 2H), 6.92-6.91 (m, 2H), 5.74-5.63 (m, 1H), 5.26-5.17 (m, 2H), 3.07 (d, J = 6.8 Hz, 2H)), 2.78 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 152.57, 146.04, 133.42, 128.62, 127.64, 127.01, 126.00, 125.32, 124.43, 121.24, 76.38, 48.81. HRMS (ESI) m/z (M+H+) calcd for $C_{14}H_{14}OS$: 230.0765, found: 230.0763.

2-phenylpent-4-en-2-ol (2g').

The title compound was obtained according to the general procedure. Yellow oil: 45 mg, 55%; IR (KBr): 3559, 3071, 2977, 1947, 1635, 1487, 1445, 1383,1069, 998, 915, 862, 766, 700, 658cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.45-7.43 (m, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.25-7.22 (m, 1H), 5.67-5.57 (m, 1H), 5.15-5.10 (m, 2H), 2.71-2.66 (m, 1H), 2.53-2.47 (m, 1H), 2.08(s, 1H)), 1.54 (s,

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3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 148.10, 134.14, 128.64, 127.08, 125.23, 119.93, 74.09, 48.93, 30.36. HRMS (ESI) m/z (M+H+) calcd for $C_{11}H_{14}O$: 162.1045, found: 162.1046.

Conclusions

In summary, we have documented the first Barbier-type reaction of allyl halides with diaryl ketones mediated by neodymium. As a complement to the traditional metal-mediated or catalyzed Barbier reactions, this reaction was highly α-regioselective and the reaction was conveniently carried out under mild conditions in a one-pot fashion. In this work, a straightforward strategy to synthesize 4-substituent homoallylic alcohols was developed. This strategy provides a broad scope and moderate to good yields of the products in a relatively short reaction time without use of any additives.

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Notes and references

(1) P. Girard, J. L. Namy and H. B. Kagan, *J. Am. Chem. SOC.* 1980, **102**, 2693.

(2) P. Girard, J. L. Namy and H. B. Kagan, *New. J. Chem.* 1977, 1; P. J. Girard, L. Namy and H. B. Kagan, *J. Am. Chem. Soc.* 1980, **102**, 2693; H. B. Kagan, *Tetrahedron*. 2003, **59**, 10351; K. Gopalaiah and H. B. Kagan, *New. J. Chem.* 2008, **32**, 607; G. A. Molander, *Chem. Rev.* 1992, **92**, 29; G. A. Molander, *Acc. Chem. Res.* 1998, **31**, 603; A. Krief and A. M. Laval, *Chem. Rev.* 1999, **99**, 745; G. A. Molander and C. R. Harris. *Tetrahedron.* 1998, **54**, 3321; G. A. Molander and C. R. Harris, *Chem. Rev.* 1996, **96**, 307; E. Hasegawa and D. P. Curran, *Tetrahedron Lett.* 1993, **34**, 1717; C. F. Sturino and A. G. Fallis, *J. Am. Chem. Soc.* 1994, **116**, 7447; M. Szostak and D. J. Procter, *Angew. Chem. Int. Ed*. 2012, **51**, 9238.

(3) W. J. Evans, P. S. Workman and N. T. Allen, *Org. Lett.* 2003, **5**, 2041; M. E. Burin, M. V. Smirnova, G. K. Fukin, E. V. Baranov and M. N. Bochkarev, *Eur. J. Inorg. Chem.* 2006, 351; A. A. Fagin, T. V. Balashova, D. M. Kusyaev, T. I. Kulikova, T. A. Glukhova, N. P. Makarenko, Y. A. Kurskii, W. J. Evans and M. N. Bochkarev, *Polyhedron*. 2006, **25**, 1105; F. Jaroschik, A. Momin, F. Nief, X. F. Le Goff, G. B. Deacon and P. C. Junk, *Angew. Chem. Int. Ed*. 2009, **48**, 1117.

(4) M. N. Bochkarev and A. A. Fagin, *Chem. Eur. J.* 1999, **5**, 2990; W. J. Evans, N. T. Allen and J. W. Ziller, *J. Am. Chem. Soc.* 2000, **122**, 11749; X. Xiang, Q. S. Shen, J. L. Wang, Z. Y. Zhu, W. Huang and X. G. Zhou, *Organometallics.* 2008, **27**, 1959.

(5) M. N. Bochkarev, I. L. Fedushkin, A. A. Fagin, T. V. Petrovskaya, J. W. Ziller, R. N. Broomhall-Dillard and W. J. Evans, *Angew. Chem. Int. Ed. Engl.* 1997, **36**, 133; W. J. Evans and N. T. Allen, *J. Am. Chem. Soc.* 2000, **122**, 2118; D. Turcitu, F. Nief and L. Ricard, *Chem. Eur. J.* 2003, **9**, 4916.

(6) M. K. Basu and B. K. Banik, *Tetrahedron Lett.* 2001, **42**, 187; R. S. Miller, J. M. Sealy, M. Shabangi, M. L. Kuhlman, J. R. Fuchs and R. Flowers A, *J. Am. Chem. Soc.* 2000, **122**, 7718; Y. Asano, S. Suzuki, T. Aoyama, K. Shimizu, M. Kajitani and Y. Yokoyama, *Synthesis.* 2007, 1309; A. Zörb and R. Brückner, *Eur. J. Org. Chem.* 2010, 4785; J. Ready, M. S. E. Reisman, M. Hirata, M. M. Weiss, K. Tamaki, T. V. Ovaska and J. L. Wood, *Angew. Chem.* 2004, **116**, 1290; S. E. Reisman, J. M. Ready, A. Hasuoka, C. J. Smith and J. L. Wood, *J. Am. Chem. Soc.* 2006, **128**, 1448; S. E. Reisman, J. M. Ready, M. M. Weiss, A. Hasuoka, M. Hirata, K. Tamaki, T. V. Ovaska, C. J. Smith and J. L. Wood, *J. Am. Chem. Soc.* 2008, **130**, 2087; S. Matsukawa and Y. Hinakubo. *Org. Lett.* 2003, **5**, 1221; G. Guazzelli, S. D. Grazia, K. D. Collins, H. Matsubara, M. Spain and D. J. Procter, *J. Am. Chem. Soc.* 2009, **131**, 7214; M. Szostak, M. Spain and D. J. Procter. *Nat. Protocols.* 2012, **7**, 970; L. A. Duffy, H. Matsubara and D. J. Procter, *J. Am. Chem. Soc.* 2008, **130**, 1136.

(7) B. A. Dolgoplosk, E. I. Tinyakova, I. N. Markevich, T. V. Soboleva, G. M. Chernenko, O. K. Sharaev and V. A. Yakovlev, *J. Organomet. Chem.* 1983, **255**, 71; H. Schumann, J. Mueller, N. Bruncks, H. Lauke, J. Pickardt, H. Schwarz and K. Eckart, *Organometallics.* 1984, **3**, 69; K. Yokoo, Y. Fujiwara, T. Fukagawa and H. Taniguchi, *Polyhedron.* 1983, **2**, 1101; H. Kawabata, T. Nishino, Y. Nishiyama and N. Sonoda, *Tetrahedron Lett.* 2002, **43**, 4911; Z. M. Hou, Y. Fujiwara, T. Jintoku, N. Mine, K. Yokoo and H. Taniguchi. *J. Org. Chem.* 1987, **52**, 3524.

(8) Z. M. Hou, Y. Fujiwara, T. Jintoku, N. Mine, K. Yokoo and H. Taniguchi. *J. Org. Chem.* 1987, **52**, 3524; T. Imamoto, T. Kusumoto, Y. Hatanaka and M. Yokoyama, *Tetrahedron Lett.* 1982, **23**, 1353; S. Fukuzawa, T. Fujinami and S. *J.* Sakai, *Chem. Soc. Chem. Commun.* 1986, **6**, 475; S. Fukuzawa, N. Sumimoto, T. Fujinami and S. Sakai. *J. Org. Chem*. 1990, **55**, 1328.

(9) (a) R. Yanada, K. Bessho and K. Yanada, *Chem. Lett.* 1994, **7**, 1279; N. Akane, T. Hatano, H. Kusui, Y. Nishiyama and Y. Ishii, *J. Org. Chem.* 1994, **59**, 7902; R. Yanada, K. Bessho and K. Yanada, *Synlett.* 1995, 1261; R. Yanada, N. Negoro, K. Yanada and T. Fujita, *Tetrahedron Lett,* 1996, **37**, 9313; R. Yanada, N. Negoro, K. Yanada and T. Fujita, *Tetrahedron Lett.* 1997, **38**, 3271; L. Wang and Y. Zhang. *Tetrahedron*. 1998, **54**, 11129.

(10) Z. Y. Zhu, J. L. Wang, Z. X. Zhang, X. Xiang and X. G. Zhou, *Organometallics.* 2007, **26**, 2499; W. F. Chen, K. B. Li, Z. Q. Hu, L. L. Wang, G. Q. Lai and Z. F. Li, *Organometallics.* 2011, **30**, 2026.

(11) Z. Hou, Y. Fujiwara and H. Taniguchi, *J. Org. Chem.*, 1988, **53**, 3118; Z. Hou, H. Taniguchi and Y. Fujiwara, *Chem. Lett.*, 1987, 305; K. Takaki, Y. Tsubaki, S. Tanaka, F. Beppu and Y. Fujiwara, *Chem. Lett.* 1990, 203; K. Takaki, F. Beppu, S. Tanaka, T. Jintoku and Y. Fujiwara, *J. Chem. Soc. Chem. Commun*, 1990, 516; K. Takaki, K. Nagase, F. Beppu and Y. Fujiwara, *Chem. Lett.* 1991, 1665.

(12) T. Nishino, Y. Nishiyama and N. Sonoda, *Heteroatom Chem.* 2000, **11**, 81; T. Nishino, Y. Nishiyama and N. Sonoda, *Heteroatom Chem.* 2002, **13**, 131; T. Nishino, T. Watanabe, M. Okada, Y. Nishiyama and N. Sonoda, *J. Org. Chem.* 2002, **67**, 966; T. Nishino, Y. Nishiyama and N. Sonoda, *Tetrahedron Lett.* 2002, **43**, 3689.

(13) Y. Y. Hu, T. Zhao and S. L. Zhang, *Chem. Eur. J.* 2010, **16**, 1697; Y. Li, Y. Y. Hu and S. L. Zhang, *Chem. Commun.* 2013, **49**, 10635; X. D. Liu, J. C. Di and S. L. Zhang, *Synthesis.* 2009, **16**, 2749; J. C. Di and S. L. Zhang, *Synlett.* 2008, **10**, 1491.

(14) S. E. Denmark and J. Fu, *Chem. Rev.* 2003, **103**, 2763; T. P. Loh, J. R. Zhou and Y. Zheng, *Org. Lett.* 1999, **1**, 1855; R. M. Moslin and T. F. Jamison, *J. Org. Chem*. 2007, **72**, 9736; C. Ma, S. Schiltz and X. F. Le Goff, *Chem.-Eur. J.* 2008, **14**, 7314;

View Article Online
DOI: 10.1039/C6RA18378F

Z. Zhang, J. Huang, B. Ma and Y. Kishi, *Org. Lett.* 2008, **10**, 3073; L. M. Fleury and B. L. Ashfeld, *Org. Lett.* 2009, **11**, 5670; P. Sinha and S. Roy, *Chem. Commun.* 2001, 1798.

(15) S. K. Woo, M. S. Kwon and E. Lee, *Angew. Chem. Int. Ed.* 2008, **47**, 3242–3244; C. L. Pereira, Y. H. Chen and F. E. McDonald, *J. Am. Chem. Soc.* 2009, **131**, 6066; M. R. Gesinski, K. Tadpetch and S. D. Rychnovsky, *Org. Lett.* 2009, **11**, 5342; O. Koepler, S. Laschat, A. Baro, P. Fischer, B. Miehlich, M. Hotfilder and C. le Viseur, *Eur. J. Org. Chem.* 2004, 3611; E. Roulland and M. S. Ermolenko, *Org. Lett.* 2005, **7**, 2225; J. Gebauer and S. Blechert, *Synlett.* 2005, **18**, 2826. J. D. Eckelbarger, J. T. Wilmot, M. T. Epperson, C. S. Thakur, D. Shum, C. Antczak, L. Tarassishin, H. Djaballah and D. Y. Gin, *Chem.-Eur. J.* 2008, **14**, 4293. K. Kamata, T. Hirano, S. Kuzuya and N. Mizuno, *J. Am. Chem. Soc.* 2009, **131**, 6997.

(16) A. Yanagisawa, s. Habaue and H. Yamamoto. *J. Am. Chem. Soc.* 1991, **113**, 8955; A. Yanagisawa, S. Habaue, K. Yasue and H. Yamamoto. *J. Am. Chem. Soc*. 1994, **116**, 6130; T. P. Loh, K. T. Tan, J. Y. Yang and C. L. Xiang, *Tetrahedron Letters.* 2001, **42**, 8701; K. T. Tan, S. S. Chng, H. S. Cheng and T. P. Loh, *J. Am. Chem. Soc.* 2003, **125**, 2958.

(17) Z. G. Zha, Z. Xie, C. L. Zhou, M. X. Chang and Z. Y. Wang, *New J. Chem.* 2003, **27**, 1297.

(18) L. M. Zhao, H. S. Jin, L. J. Wan and L. M. Zhang, *J. Org. Chem.* 2011, **76**, 1831; L. M. Zhao, L. J. Wan, H. S. Jin and S. Q. Zhang, *Eur. J. Org. Chem.* 2012, 2579.

(19) R. H. DeWolfe and W. G. Young, *Chem. Rev.* 1956, **56**, 753; G. Courtois and L. Miginiac, *J. Organomet. Chem.* 1974, **69**, 1.

(20) K. Takenaka, Y. D. Dhage and H. Sasai, *Chem. Commun.* 2013, **49**, 11224.

(21) S. X. Li, J. X Wang, X. L. Wen and X. F. Ma, *Tetrahedron*, 2011, **67**, 849.

(22) V. Kuzmin, *Zhurnal Russkago Fiziko-Khimicheskago Obshchestva*, 1910, **41**, 1314.

(23) Roesner, S, Casatejada, J. M, Elford, T. G, Sonawane, R. P and Aggarwal, V. K. *Org. Lett.* 2011, **13**, 5740.

(24) T. W. Campbell and W. G. Young, *J. Am. Chem. Soc.,* 1947, **69**, 3066.

(25) Y. Rollin, S. Derien, E. Dunach. C. Gebehenne and J. Perichon., *Tetrahedron*, 1993, **49**, 7723.

(26) B. S. Wei, H. Li, W. X. Zhang and Z. f. Xi, *Organometallics*, 2015, **34**, 1339.

(27) Y. Cui, W. Li, T. Sato, Y. Yamashita and S. Kobayashi. *Adv. Synth. Catal.* 2013, **355**, 1193.

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The first utility of neodymium as a mediating-metal in the Barbier reaction of diaryl ketones with allyl halides was reported in this paper. Contrast to traditional metal-mediated or catalyzed Barbier reactions, this reaction was highly α-regioselective and conveniently carried out under mild conditions in a one-pot fashion with moderate to good yields. The protocol constituted an availability of starting materials, wide substrate scope, operational simplicity and powerful alternative approach.