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A practical palladium catalyzed dehalogenation of aryl halides and α-haloketones

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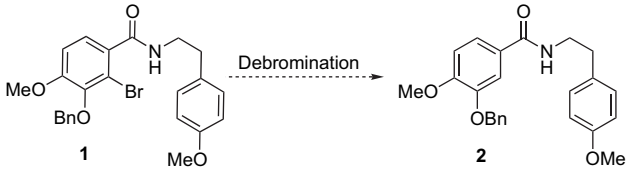
Abstract—A practical and high-yielding protocol for the dehalogenation of aromatic halides is presented. In the presence of palladium acetate, triphenylphosphine, and potassium carbonate, a number of highly functionalized aromatic halides as well as α-haloketones were dehalogenated with alcohols as hydrogen donors.

1. Introduction

A halogen atom is introduced to a given position of arene ring system in organic synthesis either as an activating group or a blocking group.[1] Occasionally, it is introduced to arene ring simply from side reactions of other desired synthetic operation.[2] Dehalogenation is an important chemical transformation in organic synthesis and in industrial applications.[3] Because aryl halides are deleterious environmental pollutants, this transformation is now assumed to be more important for decontamination of aromatic halides.[4] A great number of dehalogenation methods have been developed over years.[5] Recent advances in this field have led to several new methods by employing palladium,[6,4b] rhodium,[7] iron,[8] and nickel[9] catalysts. Although numerous reagents or protocols are available for dehalogenation, many reported methods suffered from some limitations. Functional group compatibility as well as selectivity is rarely addressed. In our work on the synthesis of galanthamine derivatives, we needed a debromination method compatible with various functional groups (Scheme 1).

It was unlikely that substrate **1** could sustain conventional hydrogenation (Pd/C, H_2) or metal hydride reduction without affecting the benzyloxyl group and the amide group. A method published in 1978 by Helquist drew our attention.[2a] A number of aryl bromides were reduced to arenes by utilization of sodium methoxide as hydrogen donor in the presence of tetrakis(triphenylphosphine)palladium in DMF



Scheme 1. Desired debromination of highly functional substrate.

(100 °C). The advantage of Helquist's method is the use of a very simple, readily available, inexpensive, and comparatively nonhazardous source of hydrogen donor. Unfortunately, utilization of Helquist's condition toward substrate **1** resulted in a complicated mixture of products. Having failed to promote the desired debromination reaction, we thus initiated a research program aiming to develop a dehalogenation process compatible with various functional groups. In this paper, we reported a practical, functional group compatible, and high-yielding protocol for the dehalogenation of aromatic halides and α-haloketones.

2. Results and discussion

Because triphenylphosphine is readily available and cheap, it was chosen as a ligand to optimize the palladium catalyzed dehalogenation. The reaction was initially carried out in 2-butanol in the presence of potassium carbonate. To our delight, desired debromination product was obtained in 98% isolated yield at 100 °C (oil bath) (Scheme 2).

Encouraged by this result, we employed 3,4,5-trimethoxyphenyl bromide as substrate to study the influence of bases

Keywords: Dehalogenation; Catalytic; Hydrogen donor; Aromatic halides; α-Haloketones.
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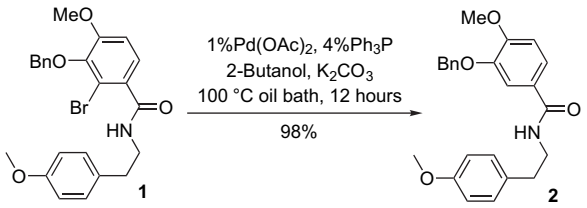
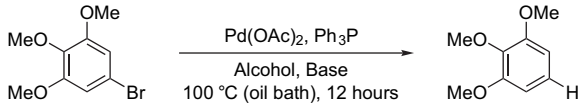


Scheme 2. Pd catalyzed debromination in 2-butanol.

Table 1. Studies on palladium catalyzed debromination of aromatic bromides[a]



Entry	Base	Hydrogen donors	Times (h)	Yield (%)
1	$NaHCO_3$	2-Butanol	1	5
2	K_2CO_3	2-Butanol	1	35
3	Cs_2CO_3	2-Butanol	1	44
4	KOH	2-Butanol	1	99
5	K_2CO_3	*iso*-Propanol	1	16
6	K_2CO_3	*n*-Butanol	1	47

[a] Yields represent isolated yields. Aryl bromide (1 mmol), $Pd(OAc)_2$ (1 mmol %), Ph_3P (4 mmol %), and K_2CO_3 (2 mmol) in commercially available alcohol (5 mL) were degassed and purged with nitrogen, then stirred at 100 °C (oil bath).

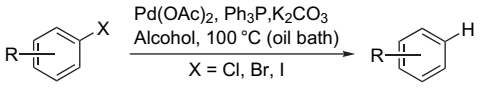
and solvents. The experimental results are shown in Table 1. The debromination reaction tended to be carried out under stronger basic condition. Utilization of *n*-butanol as a solvent enhanced the reaction rate.

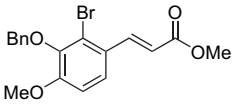
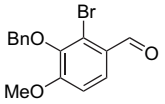
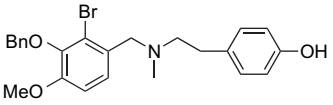
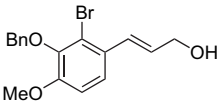
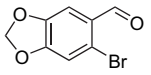
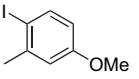
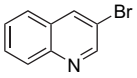
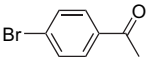
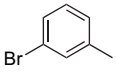
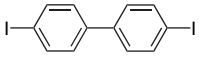
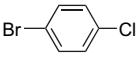
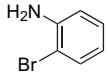
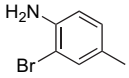
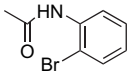
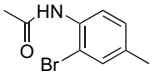
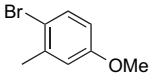
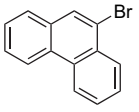
In consideration of functional group compatibility, potassium carbonate was chosen as a base and a number of aryl halides were subjected to dehalogenation in the presence of palladium acetate and triphenylphosphine. The results are summarized in Table 2. It is noteworthy that a variety of functional groups such as double bond, benzyloxyl group, carbonyl group, ester, phenol, amino group, and amide are compatible under our reaction conditions. The bromo group in 1-bromo-4-chlorobenzene or in 1-bromo-3,5-difluorobenzene could be selectively removed (see entries 11 and 24 in Table 2) in the presence of a chloro or a fluoro moiety. Deiodination and dechlorination were also achieved. It is interesting that *iso*-propanol was a better hydrogen source when halophenols were used as substrates. Dehalogenation of halophenol in *n*-butanol system led to decomposition of palladium catalysts and formation of a black precipitate. Reduction of 4-fluoroanisole was not observed under our reaction conditions.

This dehalogenation procedure could also be applied to α-haloketones. Excellent results were obtained for a number of α-haloketones. The results are shown in Table 3.

In summary, we have developed a practical and efficient method compatible with various functional groups for the dehalogenation of aryl halides and α-haloketones. The advantage of this procedure is that it is easy to handle and highly compatible with a lot of functionalities. Furthermore, triphenylphosphine ligand is readily available and inexpensive. In combination with this method, utilization of bromine

Table 2. Pd catalyzed dehalogenation of aromatic halides with alcohol as hydrogen donor



Entry	Method	Substrates	Yield (%)
1	[A]		99*
2	[A]		98
3	[A]		99
4	[A]		90
5	[A]		98
6	[A]		93
7	[A]		99
8	[A]		99
9	[A]		99
10	[A]		97
11	[A]		95
12	[B]		93
13	[B]		95
14	[B]		93
15	[B]		92
16	[B]		98
17	[B]		99

(*continued*)

Table 2. (*continued*)

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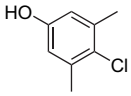
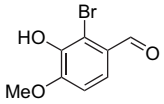
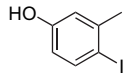
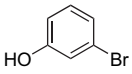
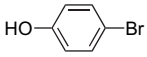
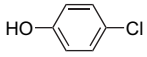
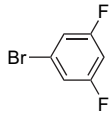
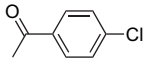
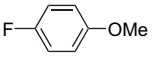
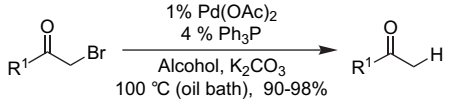
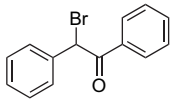
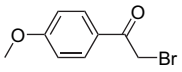
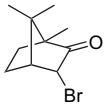
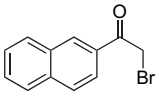
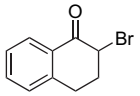
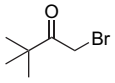
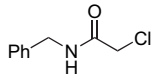
18	[B] [C]		55 92
19	[B] [C]		30 82
20	[B] [C]		50 98
21	[C]		95
22	[C]		97
23	[C]		15
24	[A]		97
25	[B]		40
26	[A], [B], [C]		Starting material

[A] Aryl halides (1 mmol), $Pd(OAc)_2$ (1 mmol %), Ph_3P (4 mmol %), and K_2CO_3 (2 mmol) in commercially available *n*-butanol (5 mL) were stirred at 100 °C (oil bath) for 1 h. [B] Aryl halides (1 mmol), $Pd(OAc)_2$ (2–5 mmol %), Ph_3P (8–20 mmol %), and K_2CO_3 (2 mmol) in commercially available *n*-butanol (5 mL) were stirred at 100 °C (oil bath) for 14 h. [C] Aryl halides (1 mmol), $Pd(OAc)_2$ (3–5 mmol %), Ph_3P (12–20 mmol %), and K_2CO_3 (2 mmol) in commercially available *iso*-propanol (5 mL) were stirred at 90 °C (oil bath) for 14 h. [*] The methyl ester was also converted to *n*-butyl ester by a transesterification process. Yields represented isolated yields or determined by GC–MS. The isolated products were characterized by ^{1}H NMR, ^{13}C NMR, and GC–MS, and all known compounds are identical to authentic samples.

Table 3. Pd catalyzed debromination of α-haloketones with *n*-butanol as hydrogen source[a]



Entry	Substrates	Yield (%)
1		90
2		92
3		92[b]
4		94
5		99
6		95
7		61[b]

[a] α-Bromoketones (1 mmol), $Pd(OAc)_2$ (1 mmol %), Ph_3P (4 mmol %), and K_2CO_3 (2 mmol) in commercially available *n*-butanol (5 mL) were stirred at 100 °C (oil bath).

[b] Substrate (1 mmol), $Pd(OAc)_2$ (2–5 mmol %), Ph_3P (8–20% mmol), and K_2CO_3 (2 mmol) in commercially available *n*-butanol (5 mL) were stirred at 100 °C (oil bath) for 14 h. Yields represented isolated yields. The isolated products were characterized by ^{1}H NMR and ^{13}C NMR, and are identical to authentic samples.

atom as a blocking group in aromatic ring system should practically be of usefulness.

3. Experimental

3.1. General experimental

Infrared (IR) spectra (ν_{max}) were recorded on a Perkin–Elmer 1800 Fourier transform infrared spectrophotometer in KBr plates. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) was recorded on Bruker Avance 300 spectrometer at 75 MHz. Chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (TMS) for all recorded NMR spectra. High-resolution mass spectra were taken on AB QSTAR Pulsar mass spectrometer. Starting materials and reagents used in reactions were obtained commercially from Acros, Aldrich, and Fluka, and were used without purification, unless otherwise indicated.

3.2. General method for palladium catalyzed dehalogenation

A mixture of palladium acetate (2.2–11 mg, 0.01–0.05 mmol), triphenylphosphine (10.5–52.5 mg, 0.04–0.20 mmol), potassium carbonate (276 mg, 2 mmol, 2.0 equiv), and aromatic halides (1 mmol) in *n*-butanol (5 mL) (*iso*-propanol was used for halophenols as substrate) was degassed and purged with nitrogen (two times). The resulting mixture was then stirred at 100 °C (oil bath) under nitrogen. The reaction was monitored by thin layer chromatography (TLC). After removal of the solvent, the residue was diluted with water (50 mL) and extracted with ethyl acetate (3×15 mL). The organic phases were combined, washed with brine (10 mL), and dried over anhydrous Na_2SO_4. The organic solvent was removed and the residue was chromatographed on silica gel to afford the products. All compounds were characterized by ^{1}H NMR and ^{13}C NMR.

3.2.1. 3-(3-Benzyloxy-2-bromo-4-methoxy-phenyl)-acrylic acid methyl ester. White solid; mp 105.4–

106.7 °C. IR (KBr) (ν_{max}, cm^{-1}): 3127 (s), 1709 (s), 1585 (m), 1487 (s), 1402 (s), 1265 (s), 1221 (s), 1027 (s), 802 (m), 733 (m). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.06 (1H, d, J=15.9 Hz), 7.56 (2H, d, J=6.6 Hz), 7.54–7.33 (4H, m), 6.90 (1H, d, J=8.7 Hz), 6.30 (1H, d, J=15.9 Hz), 5.03 (2H, s), 3.90 (3H, s), 3.81 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 167.19, 155.21, 145.75, 143.42, 137.08, 128.57, 128.47, 128.28, 128.05, 123.48, 121.99, 118.77, 111.56, 74.73, 56.31, 51.82. HRMS (ESI^+) calcd for $C_{18}H_{17}O_4NaBr$ $[M+Na]^+$: 399.0207, found: 399.0214.

3.2.2. 3-(3-Benzyloxy-4-methoxy-phenyl)acrylic acid butyl ester. White solid; mp 129.8–130.2 °C. IR (KBr) (ν_{max}, cm^{-1}): 3433 (s), 3129 (s), 1715 (m), 1635 (m), 1590 (w), 1512 (m), 1399 (s), 1265 (m), 1168 (m), 1011 (m). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.58 (1H, d, J=15.9 Hz), 7.46–7.30 (5H, m), 7.10 (1H, d, J=7.8 Hz), 7.11 (1H, s), 6.86 (1H, d, J=7.8 Hz), 6.24 (1H, d, J=15.9 Hz), 5.15 (2H, s), 4.19 (2H, t, J=6.6 Hz), 3.88 (3H, s), 1.76–1.56 (2H, m), 1.46–1.39 (2H, m), 0.96 (3H, t, J=7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 167.43, 151.89, 148.47, 144.53, 136.84, 128.74, 128.14, 127.50, 127.49, 123.00, 116.08, 112.77, 111.68, 71.19, 64.40, 56.10, 30.95, 19.34, 13.89. HRMS (ESI^+) calcd for $C_{21}H_{24}O_4Na$ $[M+Na]^+$: 363.1572, found: 363.1573.

3.2.3. 3-(3-Benzyloxy-2-bromo-4-methoxy-phenyl)prop-2-en-1-ol. White solid; mp 69.2–70.0 °C. IR (KBr) (ν_{max}, cm^{-1}): 3421 (s), 3135 (s), 3021 (s), 1634 (m), 1589 (m), 1482 (m), 1401 (s), 1290 (s), 1215 (w), 1029 (s), 963 (m), 806 (w), 744 (m). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.57 (2H, d, J=6.5 Hz), 7.40–7.31 (3H, m), 7.25 (1H, d, J=8.7 Hz), 6.91 (1H, d, J=15.8 Hz), 6.85 (1H, d, J=8.7 Hz), 6.18 (1H, dt, J=15.8, 5.8 Hz), 5.00 (2H, s), 4.31 (2H, dd, J=5.8, 1.5 Hz), 3.85 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 153.29, 145.39, 137.30, 130.48, 130.04, 130.00, 128.56, 128.42, 128.17, 122.43, 120.09, 111.72, 74.67, 63.77, 56.31. HRMS (ESI^+) calcd for $C_{17}H_{17}O_3NaBr$ $[M+Na]^+$: 371.0258, found: 371.0263.

3.2.4. 3-(3-Benzyloxy-4-methoxy-phenyl)prop-2-en-1-ol. White solid; mp 60.3–60.8 °C. IR (KBr) (ν_{max}, cm^{-1}): 3140 (s), 1590 (m), 1481 (m), 1400 (s), 1289 (s), 1265 (s), 1228 (m), 1147 (m), 1091 (w), 1008 (s), 962 (s), 802 (m), 745 (m), 697 (m). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.60–7.30 (5H, m), 7.05–6.80 (3H, m), 6.49 (1H, d, J=15.9 Hz), 6.14 (1H, dt, J=15.9, 5.8 Hz), 5.16 (2H, s), 4.27 (2H, dd, J=5.8, 1.0 Hz), 3.88 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 149.68, 148.30, 137.51, 131.18, 129.74, 128.70, 128.01, 127.43, 126.59, 120.29, 111.84, 111.76, 71.15, 63.95, 56.14. HRMS (ESI^+) calcd for $C_{17}H_{18}O_3Na$ $[M+Na]^+$: 293.1153, found: 293.1155.

3.2.5. 3-Benzyloxy-2-bromo-4-methoxy-*N*-[2-(4-methoxy-phenyl)ethyl]benzamide. White solid; mp 129.5–129.7 °C. IR (KBr) (ν_{max}, cm^{-1}): 3466 (m), 3129 (s), 3013 (m), 1640 (m), 1541 (w), 1401 (s), 1286 (w), 1256 (w), 1182 (w), 1030 (w). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.52 (2H, d, J=8.5 Hz), 7.41–7.30 (3H, m), 7.25 (1H, d, J=8.5 Hz), 7.15 (2H, d, J=8.5 Hz), 6.85 (1H, d, J=8.5 Hz), 6.83 (2H, d, J=8.5 Hz), 6.09 (1H, br s), 4.97 (2H, s), 3.85 (3H, s), 3.77 (3H, s), 3.66 (2H, q, J=6.7 Hz), 2.87 (2H, t, J=6.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 167.36, 158.48, 155.11, 145.47, 137.03, 131.16, 130.89, 129.92, 128.57, 128.49, 128.31, 125.44, 116.17, 114.24, 111.33, 74.81, 56.29, 55.41, 41.53, 34.69. HRMS (ESI^+) calcd for $C_{24}H_{25}NO_4Br$ $[M+H]^+$: 470.0966, found: 470.0969.

3.2.6. 3-Benzyloxy-4-methoxy-*N*-[2-(4-methoxy-phenyl)-ethyl]benzamide. White solid; mp 169.3–170.1 °C. IR (KBr) (ν_{max}, cm^{-1}): 3295 (m), 3128 (s), 3017 (m), 1632 (m), 1507 (s), 1400 (s), 1314 (w), 1257 (m), 1185 (w), 1137 (w), 1019 (w). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.50–7.30 (6H, m), 7.22 (1H, dd, J=8.4, 2.0 Hz), 7.13 (2H, d, J=8.6 Hz), 6.86 (2H, d, J=8.6 Hz), 6.09 (1H, br s), 5.14 (2H, s), 3.89 (3H, s), 3.79 (3H, s), 3.63 (2H, q, J=6.8 Hz), 2.84 (2H, t, J=6.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 167.03, 158.48, 152.52, 148.24, 136.80, 131.10, 129.89, 128.70, 128.13, 127.66, 127.42, 119.98, 114.26, 113.19, 111.04, 71.19, 56.17, 55.40, 41.41, 34.95. HRMS (ESI^+) calcd for $C_{24}H_{26}NO_4$ $[M+H]^+$: 392.1861, found: 392.1853.

3.2.7. (3-Benzyloxy-2-bromo-4-methoxy-benzyl)-[2-(4-hydroxy-phenyl)ethyl]methyl-amine. Colorless oil. IR (KBr) (ν_{max}, cm^{-1}): 3129 (s), 2940 (s), 1600 (s), 1481 (s), 1451 (s), 1403 (s), 1273 (s), 1031 (s), 819 (s), 740 (s). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.86 (1H, br s), 7.60 (2H, d, J=7.3 Hz), 7.45–7.30 (3H, m), 7.24 (1H, d, J=8.5 Hz), 7.04 (2H, d, J=8.2 Hz), 6.87 (1H, d, J=8.5 Hz), 6.77 (2H, d, J=8.2 Hz), 5.04 (2H, s), 3.85 (3H, s), 3.78 (2H, s), 2.92–2.73 (4H, m), 2.41 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 154.87, 152.82, 144.95, 137.04, 130.79, 129.58, 128.38, 128.18, 127.95, 126.42, 121.05, 115.50, 111.10, 74.41, 60.48, 59.44, 55.96, 41.53, 32.20. HRMS (ESI^+) calcd for $C_{24}H_{27}NO_3Br$ $[M+H]^+$: 456.1174, found: 456.1169.

3.2.8. (3-Benzyloxy-4-methoxy-benzyl)-[2-(4-hydroxy-phenyl)ethyl]methyl-amine. White solid; mp 139.2–139.8 °C. IR (KBr) (ν_{max}, cm^{-1}): 3437 (s), 3124 (s), 3009 (s), 1599 (m), 1512 (s), 1455 (m), 1398 (s), 1254 (s), 1162 (m), 1125 (m), 1010 (m), 811 (m). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.40 (2H, d, J=6.8 Hz), 7.35–7.20 (3H, m), 6.97 (2H, d, J=8.4 Hz), 6.96 (1H, s), 6.92 (2H, s), 6.75 (2H, d, J=8.4 Hz), 5.03 (2H, s), 3.84 (3H, s), 3.47 (2H, s), 2.80–2.65 (2H, m), 2.65–2.50 (2H, m), 2.22 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 155.57, 148.82, 148.06, 137.20, 131.02, 130.78, 129.76, 128.49, 127.79, 127.53, 122.08, 115.65, 114.97, 111.47, 70.78, 61.81, 59.23, 56.09, 41.87, 32.61. HRMS (ESI^+) calcd for $C_{24}H_{28}NO_3$ $[M+H]^+$: 378.2069, found: 378.2074.

3.2.9. 3-Benzyloxy-2-bromo-4-methoxy-benzaldehyde. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 10.27 (1H, s), 7.75 (1H, d, J=8.7 Hz), 7.58–7.53 (2H, m), 7.45–7.32 (3H, m), 6.97 (1H, d, J=8.7 Hz), 5.06 (2H, s), 3.95 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 191.07, 158.91, 145.35, 136.82, 128.63, 128.54, 128.44, 127.67, 126.69, 123.61, 111.13, 74.97, 56.45.

3.2.10. 3-Benzyloxy-4-methoxy-benzaldehyde. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 9.81 (1H, s), 7.50–7.42 (4H, m), 7.42–7.23 (3H, m), 6.98 (1H, d, J=8.5 Hz), 5.18 (2H, s), 3.94 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 190.91, 155.06, 148.71, 136.32, 129.99, 128.70, 128.18, 127.54, 126.98, 111.29, 110.80, 70.84, 56.22.

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