Copper nano-catalyst: sustainable phenyl-selenylation of aryl iodides and vinyl bromides in water under ligand free conditions[†]

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A simple and efficient procedure for the synthesis of aryl- and vinyl-selenides has been developed by a copper nanoparticle catalysed reaction of aryl iodide/vinyl bromide with diphenyl diselenide in the presence of zinc in water. (*E*)-Vinyl bromides produce (*E*)-vinyl selenides stereoselectively, whereas (*Z*)-vinyl bromides provide mixtures of (*E*) and (*Z*) isomers. The catalyst was recycled.

Introduction

The aryl-heteroatom bond formation is an important process and requires activation of the aryl moiety. This is usually accomplished in the presence of a transition metal.1 Organoselenium compounds in general have been the subject of renewed interest because of their potential as anticancer and antioxidant agents.² Vinyl selenides are very useful precursors in organic synthesis and are often used as intermediates in the preparation of carbonyl compounds and functionalized alkenes.3 Thus a number of methods have been developed for their synthesis.^{4,5,6} Usually, aryl selenides were prepared by the reaction of halobenzene with phenylselenol (PhSeH) or benzene selenolate anion (PhSeNa) or diphenyl diselenide (Ph-SeSePh) in the presence of a transition metal catalyst such as Pd,⁴ Ni,⁵ or Cu-salt⁶ among others.⁷ However, Cu-catalysed reactions⁶ using PhSeSePh have been of much interest, possibly because of the easy availability and low cost of copper derivatives and the easy handling of the selenium reagent. These catalysts include CuI/DMSO, 6a,6b CuI-bpy in DMSO-H2O,6c CuI/L- proline/Zn in [bmim]BF4,6d Cu2O-bpy/Mg in DMF,6e CuI/ligand/base in ionic liquid,^{6f} CuI-bpy/Al in DMF,^{6g} CuI-bpy/Mg in DMF under microwave irradiation,^{6h} CuI/neocuproine in toluene,⁶ⁱ and CuI/HMPA.^{6j} In general, all of these methods addressed either aryl selenides^{6b,6c,6e,6g,6h,6i} or vinyl selenides^{6a,6d,6f,6j} with the exception of one66 which included two examples of (E)-vinyl selenides together with aryl selenides. Recently, we reported a onepot synthesis of vinyl selenides by an InI promoted cleavage of diphenyl diselenide and subsequent Pd(0)-catalysed condensation with vinylic bromides.4a We considered it worthwhile to develop a general and simpler procedure for both aryl and vinyl selenides using a copper catalyst and diphenyl diselenide in a benign reaction media. As part of our continued activities8 towards useful transformations we report here a copper nanoparticle-catalysed synthesis of aryl and vinyl selenides by phenyl-selenylation of aryl iodides and vinyl bromides in H₂O without using any ligand (Scheme 1). The use of metal nanoparticles as efficient catalysts in organic reactions has attracted considerable interest and has undergone tremendous growth in recent times.9

[†] Electronic supplementary information (ESI) available: Copies of ¹H and ¹³C NMR spectra of all products in Table 2. See DOI: 10.1039/b819137a

 Table 1
 Reaction of iodobenzene with diphenyl diselenide using Cu nanoparticles and Zn in different solvents

Entry	Solvent	Temp. (°C)	Yield (%)
1	MeOH	65	32
2	EtOH	78	38
3	THF	66	41
4	DMF	120	78
5	H_2O	100	88



Scheme 1 Phenyl-selenylation of aryl iodides and vinyl bromides.

Results and discussion

To standardise the reaction conditions a series of reactions were performed in different solvents at varied temperatures as illustrated in Table 1. It was found that the reaction proceeds well in water under reflux giving the best yield using 20 mol% of Cu nanoparticles. With a lesser amount of Cu nanoparticles the reactions remained incomplete within a reasonable time period. Thus all reactions were carried out at 100 °C in water using 20 mol% of the Cu catalyst.

Cu nanoparticles were prepared from copper sulfate by reduction with hydrazine hydrate in ethylene glycol.¹⁰ The sizes (average diameter: 4.3 ± 0.6 nm, polydispersity index (PDI): 13.9%) of the Cu nanoparticles were determined by a Transmission Electron Microscope (TEM), (Fig. 1) and their identities were established by Energy Dispersive X-ray spectroscopy (Fig. 2), and UV spectroscopy (Fig. 3). The polydispersity index was also determined by a Dynamic Light Scattering (DLS) experiment (Fig. 4) as 13.3% and thus is in agreement with the value obtained by TEM. The increase of the particle size (hydrodynamic radii) in the DLS experiment was due to the solvation effect in solution phase.

The experimental procedure was very simple. A mixture of aryl iodide/vinyl bromide, diphenyl diselenide, Cu nanoparticles (20 mol%) and Zn dust in water was heated under reflux for a period of time as required to complete the reaction (Thin Layer Chromatography, TLC). Standard work-up and purification provided the product. Several substituted aryl iodides and vinyl

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Fig. 1 TEM image of the Cu nanoparticles.



Fig. 3 UV spectrum of the Cu nanoparticles.

bromides underwent phenyl-selenylation to produce the corresponding aryl/vinyl phenyl selenides by this procedure. The results are summarized in Table 2.

With both electron donating and electron withdrawing substituents on the aromatic ring of the aryl iodides the reaction proceeded without any difficulty. 2-Iodobenzoic acid was converted to the corresponding phenyl selenide without any damage to the carboxylic acid group. The reactions with (*E*)-styrenyl bromides (entries 8,10,12,14, Table 2) are highly stereoselective giving (*E*)-selenides. However, the (*Z*)-vinyl bromides (entries 9,11,13, Table 2) produced mixtures of (*E*)-and (*Z*)-isomers. A change of solvent from water to DMF or THF did not improve the stereoselective distribution of products. The nature of the substituents on the aromatic ring of the styrenyl bromide did not have any profound effect in the control of stereoselectivity



Fig. 4 Histogram of particle sizes obtained from the DLS experiment.

of the products. The aliphatic vinyl bromide (entry 15, Table 2) also participated in this reaction.

In general, the reactions are very clean and high yielding. Several functionalities such as OMe, NO_2 , CO_2H , CO_2Me , CF_3 and Cl are compatible with this procedure. After extraction of product, the remaining Cu nanoparticles were recycled for three more runs with a gradual loss of efficiency (Fig. 5) possibly due to the agglomerating tendency of the Cu nanoparticles during exposure in subsequent runs as shown by a TEM image of the Cu nanoparticles after the first cycle (38–59 nm) (Fig. 6). Usually, the reactivity and efficiency of nanoparticles decrease with an increase of size.¹¹



Fig. 5 Recyclability chart.



Fig. 6 TEM image of the recovered Cu nanoparticles after the first cycle.

Table 2	Synthesis of aryl/vinyl selenides using Cu nanoparticles and Zn

	R-X + 1/2 PhSe	eSePh $\frac{Cu \text{ nanoparticle}}{Zn, H_2O, reflux}$	es x R-S€	Ph	
Entry	R-X	Product	Time (h)	Yield (%) ^a	Ref.
1		SePh	10	88	6e
2	Meo	MeO	12	72	6e
3	O ₂ N	O ₂ N SePh	10	87	6e
4	CO ₂ H	SePh CO ₂ H	8	90	14
5	CO ₂ Me	SePh CO ₂ Me	8	92	6i
6	MeOC	MeOC	8	75	6i
7	F ₃ C	F ₃ CSePh	12	83	
8	Br	SePh	8	89	4a
9	Br	E : Z = 53 : 47	9	87	4a
10	Me	Me	10	87	6d
11	MeBr	Me E : Z = 32 : 68	10	86	4a
12	CI	CI-SePh	12	88	4a
13	CI	CI E : Z = 54 : 46	11	86	4a
14	MeO	MeO	8	92	4a
15	Br E : Z = 13 : 87	SePh () E : Z = 20 : 80	12	82	15

^{*a*} Yields refer to those of the purified products characterized by IR, ¹H, ¹³C NMR spectroscopic data.

In the absence of Zn dust the reaction of iodobenzene with diphenyl diselenide gave only a marginal yield (6%) of the corresponding product, whereas the reaction did not proceed at

all in the absence of Cu nanoparticles. Thus, a combination of Zn and Cu nanoparticles is essential for this reaction. Regarding the mechanism of this reaction it is suggested that Cu(0) nanoparticles, having a lower redox potential¹¹ than metallic Cu(0), undergo oxidative addition readily with diphenyl diselenide to form an intermediate, (PhSe)₂Cu(II)^{6e} (Scheme 2). On reduction by Zn this intermediate leads to the key intermediate, PhSeCu(I) which reacts with ArI to give the product ArSePh via a transient Cu(III) intermediate.^{6e,6g,6k} Support for the involvement of PhSeCu(I) in the reaction cycle was gained when it was found that PhSeCu(I), prepared separately by a different route,¹² reacts with ArI giving similar results. The CuI, generated in the reaction of PhSeCu(I) with ArI (Scheme 2), undergoes reduction by Zn to regenerate Cu(0) nanoparticles which initiate the next cycle. The Zn(SePh)₂ formed in the reduction process of Cu(SePh)₂ by Zn, reacts with CuI to give PhSeCu(I). Thus both PhSe moieties of PhSeSePh are used up in the process.



Scheme 2 Probable mechanistic pathway.

The retention of stereochemistry in the reaction of (E)-vinyl bromides and the loss of stereochemistry in (Z)-vinyl bromides may be explained as follows (Scheme 3). The Cu(III) intermediate **A** suffers a serious steric interaction between the PhSe and Ar moieties in the case of (Z)-vinyl bromides, resulting in the elimination of PhSeH to give a linear Cu(I) vinylidene complex¹³ as a transient intermediate **B**. PhSeH then undergoes re-addition



Scheme 3 Stereoselectivity in the phenyl-selenylation of vinyl bromides.

Entry	Substrate	Temp. (°C)	Time (h)	Yield (%) Metallic Cu	Yield (%) Cu NP
1		100	10	40	88
2	CO ₂ Me	100	8	38	92
3	Me	100	10	35	87
4	CI Br	100	12	43	88

 Table 3
 Comparison of the reactions of aryl iodides/vinyl bromides with

diphenyl diselenide in the presence of Cu nanoparticles and metallic copper

 Table 4
 Comparison of Cu nanoparticle catalysed phenyl-selenylation of aryl iodides and vinyl bromides with other copper catalysed methods

	Cu ₂ O, bpy, Mg ^{6e}	CuI, L-proline, Zn ^{6d}	Copper nanoparticles, Zn
Solvent	DMF	[bmim]BF₄	H ₂ O
Temp. (°C)	110	110	100
I ime (h)	18-36	24	8-12
Y 1eia (%)	53-95	08-91	12-92

to the Cu(I) vinylidene complex **B** from both stereogenic faces leading to two isomeric Cu(III) intermediates **C** and **A** which on reductive elimination provide a mixture of (E)- and (Z)-isomers. On the other hand, direct reductive elimination from intermediate **A** may lead to (Z)-vinyl selenides.

A comparative study of the reaction of aryl iodides and vinyl bromides with diphenyl diselenide using freshly prepared Cu powder and Cu(0) nanoparticles (Table 3) under identical conditions established the higher efficiency of the Cu(0) nanoparticles compared to Cu powder.

Furthermore, a comparison of the results of our procedure with those of two other related procedures using $Cu_2O/bpy/Mg^{6e}$ and CuI/L-proline/Zn^{6d} also showed a better performance by Cu(0) nanoparticles (Table 4). Interestingly, although reactions of *(E)*-vinyl bromides were addressed in a few procedures,^{6a,6d,6j} those of (Z)-vinyl bromides^{6f} were reported only in one paper (two examples).

Conclusion

In conclusion, we have developed a procedure for the efficient synthesis of unsymmetrical aryl and vinyl selenides by copper(0) nanoparticle-catalysed phenyl-selenylation of aryl iodides and vinyl bromides in the presence of Zn in water and in the absence of any ligand. The significant advantages of this procedure are simplicity in operation, neutral reaction conditions and compatibility with a variety of functional groups, general applicability to the synthesis of both aryl and vinyl selenides, excellent stereoselectivity

for (E)-vinyl selenides, high yields, recyclability of the catalyst to a certain extent and water as the reaction medium. To the best of our knowledge, this is the first report of Cu(0) nanoparticle-catalysed cross couplings of aryl iodides and vinyl bromides with diphenyl diselenide.

Experimental

IR spectra were taken as thin films for liquid compounds and as KBr pellets for solids on a FT-8300 Shimadzu spectrometer. NMR spectra were recorded on a Bruker DPX 300 instrument at 300 MHz for ¹H NMR and at 75 MHz for ¹³C NMR in CDCl₃ solutions.

Representative experimental procedure for phenyl-selenylation (entry 1, Table 2)

To a stirred mixture of Cu nanoparticles (13 mg, 0.2 mmol) and Zn dust (100 mg, 1.5 mmol) in water (2.5 mL) were added iodobenzene (204 mg, 1 mmol), and diphenyl diselenide (156 mg, 0.5 mmol). The mixture was heated to reflux (oil bath) for 10 h (TLC). After being cooled the reaction mixture was extracted with Et₂O (3×10 mL). The ether extract was washed with water and brine and dried (Na₂SO₄). The solvent was evaporated under reduced pressure to leave a crude product that was purified by column chromatography over silica gel (hexane) to afford the pure product, diphenyl selenide (206 mg, 88%) as a colourless oil. IR (neat) v_{max} /cm⁻¹ 3055, 2993, 1573, 1475, 1436, 1020. ¹H NMR (300 MHz, CDCl₃) &: 7.33–7.35 (m, 6H), 7.55–7.58 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) &: 127.4 (2C), 129.4 (4C), 131.3 (2C), 133.1 (4C). The aqueous part containing the Cu nanoparticles and zinc residue was recycled in subsequent reactions.

This procedure was followed for all the reactions listed in Table 2. All of these products except one (entry 7, Table 2) are known and have been identified by comparison of their spectroscopic data (IR, ¹H NMR and ¹³C NMR) with those reported (references in Table 2). The compounds were characterised properly by their spectroscopic data as follows:

1-Methoxy-4-phenylselanylbenzene (entry 2, Table 2)

Yield 72%, (colourless oil). IR (neat) v_{max}/cm^{-1} 3056, 2935, 1680, 1592, 1490, 1462, 1438, 1385, 1248, 1102, 1032, 1006, 735. ¹H NMR (CDCl₃, 300 MHz) δ 3.82 (s, 3H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.20–7.24 (m, 3H), 7.33–7.35 (m, 2H), 7.52 (d, *J* = 8.6 Hz, 2H). ¹³C NMR (CDCl₃, 75 MHz) δ 55.4, 115.2 (2C), 120.0, 126.6, 129.3 (2C), 131.0 (2C), 133.3, 136.7 (2C), 159.9.

1-Nitro-4-phenylselanylbenzene (entry 3, Table 2)

Yield 87% (pale yellow oil). IR (neat) v_{max}/cm^{-1} 2922, 2360, 1655, 1575, 1472, 1438, 1109, 1062, 850, 772, 737, 690. ¹H NMR (CDCl₃, 300 MHz) δ 7.33–7.45 (m, 5H), 7.61–7.64 (m, 2H), 8.02 (d, J = 8.8 Hz, 2H). ¹³C NMR (CDCl₃, 75 MHz) δ 124.0 (2C), 127.2, 129.4, 129.7 (2C), 130.1 (2C), 135.9 (2C), 144.0, 146.2.

2-Phenylselanyl-benzoic acid (entry 4, Table 2)

Yield 90% (white solid). IR (KBr) v_{max}/cm^{-1} 2972, 2871, 2827, 2659, 2563, 1670, 1583, 1556, 1460, 1415, 1313, 1282, 1259, 1151,

powder

1031, 1020, 750, 734, 682. ¹H NMR (CDCl₃, 300 MHz) δ 6.92–6.95 (m, 1H), 7.20–7.25 (m, 2H), 7.43–7.46 (m, 3H), 7.71–7.73 (m, 2H), 8.18–8.21 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ 125.0, 126.2, 128.8, 129.2, 129.4, 130.0 (2C), 132.6, 133.6, 137.7 (2C), 141.7, 172.3.

2-Phenylselanylbenzoic acid methyl ester (entry 5, Table 2)

Yield 92% (colourless oil). IR (neat) v_{max}/cm^{-1} 3055, 3014, 2997, 2949, 1708, 1583, 1560, 1303, 1273, 1253, 1141, 1101, 738, 692. ¹H NMR (CDCl₃, 300 MHz) δ 3.96 (s, 3H), 6.89–6.92 (m, 1H), 7.14–7.19 (m, 2H), 7.40–7.45 (m, 3H), 7.69–7.71 (m, 2H), 8.02–8.05 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ 52.7, 125.2, 127.5, 129.3, 129.4, 129.6, 130.2 (2C), 131.7, 133.0, 138.0 (2C), 140.9, 167.7.

1-(4-Phenylselanylphenyl) ethanone (entry 6, Table 2)

Yield 75% (pale yellow solid). IR (KBr) v_{max}/cm^{-1} 3054, 2995, 1678, 1581, 1468, 1432, 1393, 1268, 1057, 1002, 956, 819, 747, 690. ¹H NMR (CDCl₃, 300 MHz) δ 2.53 (s, 3H), 7.33–7.37 (m, 5H), 7.56–7.59 (m, 2H), 7.77 (d, J = 8.4 Hz, 2H). ¹³C NMR (CDCl₃, 75 MHz) δ 26.5, 128.4, 128.6 (2C), 128.9 (2C), 129.7 (2C), 130.3 (2C), 135.1 (2C), 140.3, 197.3.

1-Phenylselanyl-3-trifluoromethyl-benzene (entry 7, Table 2)

Yield 83% (Pale yellow oil). IR (neat) v_{max}/cm^{-1} 3060, 2927, 1577, 1477, 1421, 1321, 1166, 1128. ¹H NMR (CDCl₃, 300 MHz) δ : 7.26–7.40 (m, 4H), 7.47–7.68 (m, 5H). ¹³C NMR (CDCl₃, 75 MHz) δ : 135.18, 134.0 (2C), 133.1, 129.6 (2C), 129.5, 129.4, 128.5, 128.2, 125.5, 123.7, 121.9. HRMS Calc. for C₁₃H₉F₃SeNH₃⁺ (M⁺+NH₃): 319.0087, Found: 318.8902.

(E)-2-Phenylselanyl-vinyl benzene (entry 8, Table 2)

Yield 89% (colourless oil). IR (neat) v_{max}/cm^{-1} 3050, 1585, 1476. ¹H NMR (CDCl₃, 300 MHz) δ 6.88 (d, J = 15.7 Hz, 1H), 7.16– 7.33 (m, 9H), 7.54–7.57 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz) δ 119.5, 126.2 (2C), 127.6, 127.8 (2C), 128.8 (2C), 129.5 (2C), 130.3, 132.7, 135.3, 137.1.

Mixture of (*E*)- and (*Z*)-2-phenylselanyl-vinyl benzene (entry 9, Table 2)

Yield 87% (colourless oil). IR (neat) v_{max}/cm^{-1} 3050, 1579, 1477. ¹H NMR (CDCl₃, 300 MHz) δ 6.80 (d, J = 10.3 Hz, 1H), 6.89 (d, J = 15.7 Hz, 1H), 6.99 (d, J = 10.3 Hz, 1H), 7.17–7.42 (m, 17H), 7.55–7.59 (m, 4H). ¹³C NMR (CDCl₃, 75 MHz) δ 119.5, 124.1, 126.1 (2C), 127.3, 127.5, 127.7 (4C), 128.4 (2C), 128.5 (2C), 128.7 (2C), 129.3 (4C), 130.2 (2C), 131.7, 132.6, 132.8, 135.2, 137.1, 137.3.

(E)-1-Methyl-4-(2-phenylselanylvinyl)-benzene (entry 10, Table 2)

Yield 87% (colourless oil). IR (neat) v_{max}/cm^{-1} 3049, 3020, 1575, 1508, 1475, 1435. ¹H NMR (CDCl₃, 300 MHz) δ 2.37 (s, 3H), 6.92 (d, J = 15.7 Hz, 1H), 7.13–7.18 (m, 3H), 7.26–7.35 (m, 5H), 7.56–7.59 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz) δ 21.3, 117.9, 126.1 (2C), 127.3, 129.4 (2C), 129.5 (2C), 130.6, 132.4 (2C), 134.4, 135.8, 137.7.

Mixture of (*E*)- and (*Z*)-1-methyl-4-(2-phenylselanylvinyl)benzene (entry 11, Table 2)

Yield 86% (pale yellow oil). IR (neat) v_{max}/cm^{-1} 3015, 1634, 1640. ¹H NMR (CDCl₃, 300 MHz) δ 2.22 (s, 3H), 2.26 (s, 3H), 6.62 (d, *J* = 10.3 Hz, 1H), 6.77 (d, *J* = 15.7 Hz, 1H), 6.85 (d, *J* = 10.3 Hz, 1H), 6.99–7.23 (m, 15H), 7.42–7.49 (m, 4H). ¹³C NMR (CDCl₃, 75 MHz) δ 21.3, 21.4, 117.8, 122.8 (2C), 126.1 (2C), 127.3, 127.6 (2C), 128.3 (2C), 129.1 (2C), 129.3 (4C), 129.4, 130.1, 130.5, 131.8, 132.3, 132.7 (2C), 134.3, 134.5, 137.2 (2C), 137.7.

(E)-1-Chloro-4-(2-phenylselanylvinyl)-benzene (entry 12, Table 2)

Yield 88% (pale yellow oil). IR (neat) v_{max}/cm^{-1} 3028, 1575, 1488, 1436. ¹H NMR (CDCl₃, 300 MHz) δ 6.89 (d, J = 15.7 Hz, 1H), 7.26–7.47 (m, 8H), 7.66–7.69 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz) δ 120.8, 127.3 (2C), 127.8, 128.9 (2C), 129.5 (3C), 129.8, 132.9 (2C), 133.3, 135.6.

Mixture of (*E*)- and (*Z*)-1-chloro-4-(2-phenylselanylvinyl)-benzene (entry 13, Table 2)

Yield 86% (pale yellow oil). IR (neat) v_{max}/cm^{-1} 3028, 1488, 734. ¹H NMR (CDCl₃, 300 MHz) δ 6.60–6.69 (m, 2H), 6.77 (d, J =10.4 Hz, 1H), 7.00–7.21 (m, 15H), 7.40–7.49 (m, 4H). ¹³C NMR (CDCl₃, 75 MHz) δ 120.7, 125.0, 127.2 (2C), 127.7, 127.8, 128.6 (2C), 128.8 (4C), 129.4 (2C), 129.4 (2C), 129.5, 129.7, 130.9, 131.3, 132.8 (2C), 132.9 (2C), 133.1, 133.2, 135.5, 135.7.

(E)-1-Methoxy-4-(2-phenylselanylvinyl)-benzene (entry 14, Table 2)

Yield 92% (colourless oil). IR (neat) v_{max}/cm^{-1} 3029, 1432, 732. ¹H NMR (CDCl₃, 300 MHz) δ 3.72 (s, 3H), 6.76–6.82 (m, 3H), 6.94 (d, *J* = 15.6 Hz, 1H), 7.19–7.24 (m, 5H), 7.43–7.46 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz) δ 55.4, 114.2 (2C), 116.0, 127.2, 127.5 (2C), 129.4 (2C), 130.0, 130.9, 132.1 (2C), 136.0, 159.5.

Mixture of (*E*)- and (*Z*)-Undec-1-enylselanylbenzene (entry 15, Table 2)

Yield 82% (pale yellow oil). IR (neat) v_{max}/cm^{-1} 2954, 2923, 2852, 1577, 1477, 1436, 734. ¹H NMR (CDCl₃, 300 MHz) δ 0.90 (t, *J* = 6.7 Hz, 6H), 1.29–1.45 (m, 28H), 2.13–2.23 (m, 4H), 6.03–6.15 (m, 2H), 6.37–6.46 (m, 2H), 7.26–7.30 (m, 6H), 7.45–7.50 (m, 4H). ¹³C NMR (CDCl₃, 75 MHz) δ 13.2 (2C), 21.8 (2C), 28.0 (2C), 28.2, 28.3, 28.4, 28.6 (2C), 28.7 (2C), 30.3 (2C), 31.0 (2C), 33.4, 115.0, 119.1, 125.7, 125.8 (2C), 128.2 (4C), 130.4 (2C), 130.8 (2C), 134.6 (2C), 139.9.

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