

Hz, the noise floor is about 0.15 nG/Hz<sup>1/2</sup>. The experimental pulse sequence is shown in FIG. 7(c).

**[0067]** Single shot, zero-field PHIP spectra of ethylbenzene-β<sup>13</sup>C (labelled <sup>13</sup>CH<sub>3</sub> group), and ethylbenzene-α<sup>13</sup>C (labelled <sup>13</sup>CH<sub>2</sub> group), synthesized from labelled styrene, as obtained via the present invention, are shown in black in FIGS. 8(a) and (b), respectively. The ethylbenzene molecule is shown in the inset, with the blue carbon indicating the β label, and the green carbon indicating the α label. The spectrum of ethylbenzene-β<sup>13</sup>C in FIG. 8(a) can be understood in terms of the discussion above, with multiplets at <sup>1</sup>J<sub>HC</sub> and 2□<sup>1</sup>J<sub>HC</sub>, and additional lines at low frequency. Here the superscript indicates the number of bonds separating the interacting pair, and for ethylbenzene-β<sup>13</sup>C, <sup>1</sup>J<sub>HC</sub>=126.2 Hz<sup>26</sup>. Isolated lines in the complex spectrum fit to complex Lorentzians with half-width-at-half-maximum (HWHM) of about 0.1 Hz. It should be noted that this spectrum is similar to the correspondingly labelled ethanol-β<sup>13</sup>C spectrum reported in McDermott<sup>4</sup>, although careful inspection reveals small splittings of some lines due to long-range (at least four-bond) homonuclear couplings to protons on the benzene ring. The blue trace shows the result of a numerical simulation accounting for eight spins, including the six spins on the ethyl part of the molecule and the two nearest protons on the benzene ring. The simulation reproduces most of the features of the experimental spectrum quite well, including small splittings of several lines.

**[0068]** The zero-field PHIP spectrum of ethylbenzene-α<sup>13</sup>C shown in FIG. 8(b) is qualitatively similar to the zero-field spectrum of ethanol-α<sup>13</sup>C [4], with a multiplet at roughly 3/2□<sup>1</sup>J<sub>HC</sub> (<sup>1</sup>J<sub>HC</sub>=126.2 Hz, measured in house with a 300 MHz spectrometer) and features at low frequency. Many additional lines in the spectrum indicate that long-range couplings to the protons on the benzene ring are important. Since the ethanol-β<sup>13</sup>C spectrum does not display such complexity, the largest perturbation to the ethyl part of the molecule must be due to three-bond <sup>3</sup>J<sub>HC</sub> couplings. The green trace shows the result of numerical simulation, consisting of the six spins on the ethyl part of the molecule and the two nearest protons on the benzene ring. Simulation again reproduces most of features of the experimental spectrum, although careful inspection shows a number of additional splittings in the experimental spectrum, indicating that couplings to more remote spins on the benzene ring not included in the simulation, are important. It is worth emphasizing that, despite the similarity of the one-bond heteronuclear J-couplings, the spectra associated with different isotopomers display strikingly different features, which appear in different parts of the spectrum, facilitating easy assignment of isotopomers to their respective peaks.

**[0069]** FIG. 8 shows a single-shot zero-field PHIP J-spectra (imaginary component) of ethylbenzene-β<sup>13</sup>C (a) and ethylbenzene-α<sup>13</sup>C (b), polarized via addition of parahydrogen to labelled styrene, as obtained via the present invention. The inset shows the ethylbenzene molecule with the β and α positions indicated by the blue and green carbons, respectively. The blue and green traces in FIG. 8(a) and FIG. 8(b), respectively, are the results of numerical simulations.

**[0070]** The sensitivity of the magnetometer and the degree of parahydrogen induced polarization are sufficient to detect J-spectra in compounds with <sup>13</sup>C in natural abundance, in accordance with an exemplary embodiment of the present invention. FIG. 9 shows the zero-field PHIP spectrum of ethylbenzene with <sup>13</sup>C in natural abundance, obtained in just

eight transients via the present invention. The spectrum shown in FIG. 9 is the sum of spectra associated with the α and β isotopomers shown in FIG. 8, as well as isotopomers that carry <sup>13</sup>C in one of four non-equivalent positions on the benzene ring. The high frequency parts of the spectrum arising from the α and β isotopomers are highlighted in green and blue, respectively. The part of the signal arising from the benzene ring with a single <sup>13</sup>C is a multiplet centred about the one-bond coupling frequencies (typically about 156 Hz in aromatic systems), and also a multiplet in the low-frequency range. The high-frequency component is highlighted in red. Interestingly, spectra associated with the α or β isotopomers do not overlap with spectra associated with isotopomers with a <sup>13</sup>C on the benzene ring. It is also noteworthy that if the hydrogenation is performed in high field, large chemical shift differences between protons on the benzene ring and the parahydrogen derived protons would inhibit the transfer of polarization to the benzene ring.

**[0071]** FIG. 9 shows a zero-field J-spectrum (imaginary component) of ethylbenzene, produced via parahydrogenation of styrene with <sup>13</sup>C in natural abundance, as obtained via the present invention. These data result from averaging 8 transients following a pulse of magnetic field in the z direction with η≈π/2. The high frequency components of the signals arising from the α and β isotopomers are easily recognizable from the spectra shown in FIG. 8, and are highlighted by the green and blue bands, respectively. The signal in the neighborhood of 156 Hz is due to isotopomers with <sup>13</sup>C on the benzene ring, and is highlighted in red.

**[0072]** To further illustrate the capabilities of zero-field PHIP as a method for chemical fingerprinting in accordance with an exemplary embodiment of the present invention, spectra obtained from several different hydrogenation reactions are presented in FIG. 10(a) phenyl propyne (forming phenyl propene upon hydrogenation) with a labelled <sup>13</sup>CH<sub>3</sub> group, FIG. 10(b) dimethyl acetylenedicarboxylate (dimethyl maleate) with <sup>13</sup>C in natural abundance, and FIG. 10(c) 3-hexyne (hexene and hexane) with <sup>13</sup>C in natural abundance. These spectra in FIG. 10 are the result of averaging 1, 6, and 32 transients respectively. The phenyl propene spectrum displays characteristics similar to the ethylbenzene-β<sup>13</sup>C spectrum, although the phase and splitting pattern is clearly different since neither of the parahydrogen derived protons are part of the labelled group. The dimethyl maleate spectrum shown in FIG. 10(b) is the superposition of two different <sup>13</sup>C isotopomers, and can approximately be understood as follows: For a three-spin system, where one of the parahydrogen derived spins has a strong coupling to a <sup>13</sup>C nucleus, one can show that the spectrum consists of two lines centred around the strong coupling frequency, and an additional low frequency peak.

**[0073]** The antiphase lines centred about 165 Hz in FIG. 10(b) correspond to the isotopomer where the <sup>13</sup>C is directly bonded to one of the parahydrogen derived spins, and is accompanied by a contribution at low frequency. The other three-spin isotopomer, where the strongest coupling to the <sup>13</sup>C nucleus is through two bonds, nominally gives rise to three lines at low frequency. There are some residual splittings in the low-frequency part of the spectrum, which will be the subject of future investigation. The spectrum obtained in the hexyne reaction in FIG. 10(c) is the sum of three different <sup>13</sup>C isotopomers. For labelled <sup>13</sup>CH<sub>3</sub> groups, signal arises at <sup>1</sup>J<sub>HC</sub> and 2×<sup>1</sup>J<sub>HC</sub>, where <sup>1</sup>J<sub>HC</sub>≈125 Hz. For labelled <sup>13</sup>CH<sub>2</sub> groups, the contribution to the signal is centred about 3 J/2,