### **Supplementary Information**

for the article entitled

### Electron Ionization–Induced Release of Coded Isotopic Reporter Ions in an *m/z* Zone of Minimal Interference for Quantifiable, Multiplexed GC-MS Analyses

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*N*-(2-hydroxyethoxy)phthalimide (4). To 2-bromoethanol (3.00 g, 24.00 mmol) in DMF (15 mL) at room temperature were added *N*-hydroxyphthalimide (4.30 g, 26.35 mmol) and triethylamine (3.71 mL, 26.40 mmol). The reaction mixture then was stirred at 75 °C for 24 h whereupon the reaction was allowed to cool to room temperature and then diluted by addition of Et<sub>2</sub>O (20 mL). The resulting solution was filtered to remove the precipitated triethylamine salt, and the filtrate was concentrated by rotary evaporation. The resulting paste was dissolved in EtOAc (70 mL) and washed successively with saturated aq. NaHCO<sub>3</sub> until the aqueous layer remained clear, and then brine (2 X 10 mL). The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent was removed by rotary evaporation to afford phthalimide **4** (3.65 g, 73%) as a pale yellow solid, mp. 74-76 °C, (lit. 82-84 °C) having spectral characteristics in agreement with published data.<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (m, 2H), 7.76 (m, 2H), 4.28 (t, *J* = 4.4 Hz, 2H), 3.79 (t, *J* = 4.4 Hz, 2H), 3.51 (br s, 1H); <sup>13</sup>C NMR (100 MHz)  $\delta$  164.6, 135.0, 128.9, 124.0, 80.1, 59.7.

<sup>1.</sup> Xu, Y.; Suzuki, Y.; Lönnberg, T.; Komiyama, M. J. Am. Chem. Soc. 2009, 131, 2871-2874.

**2-((1,3-dioxoisoindolin-2-yl)oxy)ethyl 3,3,3-**<sup>2</sup>**H**<sub>3</sub>**-propionate (5a)**. To phthalimide **4** (1.48 g, 7.13 mmol) in dichloromethane (8 mL) at room temperature was added 3,3,3-<sup>2</sup>H<sub>3</sub>-propionic acid (0.5 g, 6.48 mmol). After cooling the resulting solution to 0 °C, *N*,*N*<sup>\*</sup>-diisopropylcarbodiimide (1.5 mL, 9.72 mmol) and DMAP (cat.) were added. The reaction mixture was stirred at 0 °C for 5 min, and then allowed to warm to room temperature. After stirring at room temperature for 1h the reaction mixture was filtered and the filtrate was concentrated by rotary evaporation. The crude residue was purified by column chromatography (SiO<sub>2</sub>, dichloromethane:hexane:ethyl acetate, 3:1:1 v/v, *R<sub>f</sub>*= 0.62) to afford ester **5a** (1.30 g, 76% yield) as a white solid, mp. 56.5-58.5 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (m, 2H), 7.75 (m, 2H), 4.42 (s, 4H), 2.33 (s, 2H) [the signal at  $\delta$  1.65 ppm is due to slight water contamination, see spectrum]; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  174.5, 163.5, 134.8, 129.0, 123.8, 76.0, 61.9, 27.3; FT-ICR-MS (ESI<sup>+</sup>, *m/z*) calcd for C<sub>13</sub>H<sub>11</sub>D<sub>3</sub>NO<sub>5</sub>, [M + H]<sup>+</sup> 267.1055, found 267.1058.



2-((1,3-dioxoisoindolin-2-yl)oxy)ethyl 3-<sup>13</sup>C<sub>1</sub>-3,3,3-<sup>2</sup>H<sub>3</sub>-propionate (5b). Using the general procedure outlined for the synthesis of ester 5a, phthalimide 4 (1.07 g, 5.16 mmol) was reacted with 3-<sup>13</sup>C<sub>1</sub>-3,3,3-<sup>2</sup>H<sub>3</sub>-propionic acid (0.366 g, 4.69 mmol), *N*,*N*<sup>2</sup>-diisopropylcarbodiimide (1.09 mL, 7.03 mmol) and DMAP (cat.) to afford ester 5b (1.13g, 90% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (m, 2H), 7.75 (m, 2H), 4.42 (s, 4H), 2.33 (d, *J* = 3.6 Hz, 2H) [the signal at  $\delta$  1.65

ppm is due to slight water contamination, see spectrum]; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  174.5, 163.5, 134.8, 129.0, 123.8, 76.9, 76.1, 61.9, 27.5, 27.1, 9.0-7.8 (m) [the multiplet at  $\delta$  18.1 is due to the presence of the doubly labeled isobutyrate analog (<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>R in less than < 0.5%, see spectrum]; FT-ICR-MS (ESI<sup>+</sup>, *m/z*) calcd for C<sub>12</sub><sup>13</sup>CH<sub>11</sub>D<sub>3</sub>NO<sub>5</sub>, [M + H]<sup>+</sup> 268.1088, found 268.1095.



**2-((1,3-dioxoisoindolin-2-yl)oxy)ethyl 2,3-**<sup>13</sup>C<sub>2</sub>**-3,3,3-**<sup>2</sup>H<sub>3</sub>**-propionate (5c)**. Using the general procedure outlined for the synthesis of ester **5a**, phthalimide **4** (1.03 g, 4.99 mmol) was reacted with 2,3-<sup>13</sup>C<sub>2</sub>-3,3,3-<sup>2</sup>H<sub>3</sub>-propionic acid (0.33 g, 4.15 mmol), *N*,*N*<sup>2</sup>-diisopropylcarbodiimide (0.96 mL, 6.23 mmol) and DMAP (cat.) to afford ester **5c** (0.96 g, 87% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (m, 2H), 7.75 (m, 2H), 4.42 (s, 4H), 2.33 (dd, *J* = 4.2, 128.4 Hz, 2H) [the signal at  $\delta$  1.65 ppm is due to slight water contamination, see spectrum]; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  163.5, 134.8, 129.0, 123.8, 76.1, 61.9, 27.8-27.1 (m), 9.1-7.6 (m); FT-ICR-MS (ESI<sup>+</sup>, *m/z*) calcd for C<sub>11</sub><sup>13</sup>C<sub>2</sub>H<sub>10</sub>D<sub>3</sub>NNaO<sub>5</sub>, [M + Na]<sup>+</sup> 291.0941, found 291.0959.



**2-(aminooxy)ethyl 3,3,3-**<sup>2</sup>**H**<sub>3</sub>-**propionate (AEP-32)**. To ester **5a** (1.30 g, 4.90 mmol) in dichloromethane (10 mL) at 0 °C was added methylhydrazine (284  $\mu$ L, 5.38 mmol). After stirring at 0 °C for 45 min, the reaction mixture was filtered and the filtrate was concentrated by rotary evaporation. The crude residue was passed through a short column of SiO<sub>2</sub>, eluting with dichloromethane:methanol 95:5 v/v ( $R_f = 0.47$ ), to afford a light yellow liquid. Kugelrohr

distillation of the product (5 mmHg, collect at 80 °C) afforded **AEP-32** (0.56 g, 84% yield) as a clear liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.29 (br. s, 2H), 4.28 (t, *J* = 4.4 Hz, 2H), 3.83 (t, *J* = 4.4 Hz, 2H), 2.33 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  174.8, 73.7, 62.1, 27.4; IR (neat) 3324, 1729, 1590, 1461, 1180, 1080, 1046 cm<sup>-1</sup>; FT-ICR-MS (ESI<sup>+</sup>, *m/z*) calcd for C<sub>5</sub>H<sub>9</sub>D<sub>3</sub>NO<sub>3</sub>, [M + H]<sup>+</sup> 137.1000, found 137.1000.

**2-(aminooxy)ethyl 3-**<sup>13</sup>C<sub>1</sub>**-3,3,3-**<sup>2</sup>H<sub>3</sub>**-propionate (AEP-33)**. Using the general procedure for the synthesis of AEP-32, ester **5b** (1.29 g, 4.84 mmol) was reacted with methylhydrazine (280  $\mu$ L, 5.33 mmol) to afford **AEP-33** (0.514 g, 77% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.52 (br. s, 2H), 4.30 (t, *J* = 4.4 Hz, 2H), 3.84 (t, *J* = 4.4 Hz, 2H), 2.35 (d, *J* = 3.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  174.8, 73.7, 62.1, 27.6, 27.3, 9.1-7.9 (m) [the multiplet at  $\delta$  18.2 is due to the presence of the doubly labeled isobutyrate analog (<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>R in less than < 0.5%, see spectrum]; FT-ICR-MS (ESI<sup>+</sup>, *m/z*) calcd for C<sub>4</sub><sup>13</sup>CH<sub>9</sub>D<sub>3</sub>NO<sub>3</sub>, [M + H]<sup>+</sup> 138.1034, found 138.1033.

$$D_3C_{*}O^{-NH_2}$$

**2-(aminooxy)ethyl 2,3-**<sup>13</sup>C<sub>2</sub>**-3,3,3-**<sup>2</sup>H<sub>3</sub>**-propionate (AEP-34)**. Using the general procedure for the synthesis of AEP-32, ester **5c** (0.95 g, 3.55 mmol) was reacted with methylhydrazine (205  $\mu$ L, 3.90 mmol) to afford **AEP-34** (0.404 g, 83% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.52 (br. s, 2H), 4.29 (t, *J* = 4.4 Hz, 2H), 3.83 (t, *J* = 4.4 Hz, 2H), 2.35 (dd, *J* = 3.6, 128.4 Hz, 2H) [the

signal at  $\delta$  1.61 ppm is due to slight water contamination, the signal at  $\delta$  5.29 ppm is due to CH<sub>2</sub>Cl<sub>2</sub> contamination; see spectrum]; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  73.7, 62.1, 27.6- 27.3 (m), 9.1-7.9 (m); FT-ICR-MS (ESI<sup>+</sup>, *m/z*) calcd for C<sub>3</sub><sup>13</sup>C<sub>2</sub>H<sub>9</sub>D<sub>3</sub>NO<sub>3</sub>, [M + H]<sup>+</sup> 139.1067, found 139.1069.

### **II. Proof of Concept**

#### A. General Procedure for Sample Mixture Derivatization.

The sample mixtures A, B and C were prepared (see below) and derivatized by treatment with an excess (~4 equiv) of reagents AEP-32, AEP-33, and AEP-34, respectively, to afford the derivatized mixtures A<sub>32</sub>, B<sub>33</sub>, and C<sub>34</sub>. The resultant mixtures A<sub>32</sub>, B<sub>33</sub> and C<sub>34</sub> were combined and an aliquot (50 µL) from the combined mixture was directly injected into the GC-MS instrument for analysis. All GC-MS analyses were performed using an Agilent Technologies GC-MS instrument (Agilent Technologies, Palo Alto, CA); GC component: Agilent 7820A gas chromatograph, MS component: Agilent 5975 Series MSD. The GC-MS instrument was fitted with a HP-5MS chromatographic column 30 m long with an internal diameter of 250  $\mu$ m and a stationary-phase film thickness of 0.25  $\mu$ m. High-purity helium was used as the carrier gas at a flow rate of 1.0 mL/min. The starting column oven temperature was 60 °C with a ramp of 20 °C/min to a maximum temperature of 315 °C and then held at this temperature for 2 min. The combined mixture of derivatized carbonyl substrates was examined using a 120-s solvent delay. The 1  $\mu$ L of sample solution was injected in the split mode of injection at a ratio of 10:1. The inlet temperature was set at 275 °C and the transfer line at 250°C. The ion MS source was held at 230 °C and the MS Quad at 150 °C. The detector voltage was set at 1200 V, and the electron energy for ionization was set at 70 eV. Mass spectra were collected from 25 to 400 m/z. The A-C sample mixtures were prepared, derivatizated and then analyzed by GC-MS a total of three times.

#### Sample Mixture Preparation

**Sample Mixture A**. To a solution mixture consisting of hexanal (100  $\mu$ L of a 0.66 M solution), 1-naphthaldehyde (300  $\mu$ L of a 0.60 M solution), 2-heptanone (100  $\mu$ L of a 0.84 M solution), 1methyl-4-piperidone (500  $\mu$ L of a 0.60 M solution), tetrahydro-4H-pyran-4-one (200  $\mu$ L of a 0.58 M solution), and 2-indanone (500  $\mu$ L of a 0.40 M solution), total volume 1.7 mL, was added dichloromethane (300  $\mu$ L) to generate a sample mixture A (2.0 mL).

**Derivatized Mixture A**<sub>32</sub>. To a 100  $\mu$ L aliquot of sample mixture A at room temperature was added AEP-32 (23  $\mu$ L). After incubation at room temperature 48h, the dichloromethane was removed by rotary evaporation and the resultant mixture of oxime ethers was redissolved in dichloromethane (1.0 mL) to generate derivatized mixture A<sub>32</sub>.

**Sample Mixture B**. To a solution mixture consisting of hexanal (100  $\mu$ L of a 0.66 M solution), 1-naphthaldehyde (100  $\mu$ L of a 0.60 M solution), 2-heptanone (300  $\mu$ L of a 0.84 M solution), 1methyl-4-piperidone (500  $\mu$ L of a 0.60 M solution), tetrahydro-4H-pyran-4-one (100  $\mu$ L of a 0.58 M solution), and 2-indanone (300  $\mu$ L of a 0.40 M solution), total volume 1.4 mL, was added dichloromethane (600  $\mu$ L) to generate a sample mixture B (2.0 mL).

**Derivatized Mixture B**<sub>33</sub>. To a 100  $\mu$ L aliquot of sample mixture B at room temperature was added AEP-33 (21  $\mu$ L). After incubation at room temperature 48h, the dichloromethane was removed by rotary evaporation and the resultant mixture of oxime ethers was redissolved in

dichloromethane (1.0 mL) to generate derivatized mixture B<sub>33</sub>.

**Sample Mixture C**. To a solution mixture consisting of hexanal (100  $\mu$ L of a 0.66 M solution), 1-naphthaldehyde (100  $\mu$ L of a 0.60 M solution), 2-heptanone (100  $\mu$ L of a 0.84 M solution), 1-methyl-4-piperidone (100  $\mu$ L of a 0.60 M solution), tetrahydro-4H-pyran-4-one (200  $\mu$ L of a 0.58 M solution), and 2-indanone (100  $\mu$ L of a 0.40 M solution), total volume 0.7 mL, was added dichloromethane (1.3 mL) to generate a sample mixture C (2.0 mL).

**Derivatized Mixture C**<sub>34</sub>. To a 100  $\mu$ L aliquot of sample mixture C at room temperature was added AEP-34 (11  $\mu$ L). After incubation at room temperature 48h, the dichloromethane was removed by rotary evaporation and the resultant mixture of oxime ethers was redissolved in dichloromethane (1.0 mL) to generate derivatized mixture C<sub>34</sub>.

#### **B.** Ion Count Averages and Accuracy Determination

The following table summarizes the averages, calculated from three separate experiments, for the MST ion counts, accuracy (% error) and the standard deviation. Total average error was calculated at  $4.9\% \pm 0.3\%$ .

Carbonyl Substrate	MST	Actual A,B,C Ratio	Accuracy	(% error)	Norm average i	alized on count	Standard deviation	
	(m/z)		Ζ	Ε	Ζ	Ε	Ζ	Ε
	32	1	4.16	2.47	10.85	9.34	0.55	0.45
hexanal	33	1	3.52	5.23	10.05	8.65	0.14	0.13
	34	1	1.18	2.96	10.35	9.4	0.35	0.31
1 1/1	32	3	3.82	4.46	10.74	8.16	0.47	0.26
l-naphth- aldehyde	33	1	4.42	4	3.83	2.95	0.25	0.11
aldenyde	34	1	8.54	9.72	4.04	3.12	0.21	0.15
	32	1	6.24	4.82	3.05	2.44	0.45	0.43
2-heptanone	33	3	4.05	3.7	8.24	6.69	0.65	0.74
	34	1	5.9	6.29	3.04	2.47	0.39	0.41
totus has due ATT	32	2	3		13.09		0.98	
tetranyaro-4H-	33	1	4.3		6.87		0.18	
pyrun + one	34	2	3 13.09   4.3 6.87   3.45 12.96	0.	0.15			
1	32	5	3.16		11.91		0.28	
niperidone	33	5	5.21		10.98		0.34	
piperidone	34	1	11.95		2.59		0.1	
	32	5	2.34		5.47		0.21	
2-indanone	33	3	2.8	39	3.26		0.1	
	34	1	9.67		1.21		0.05	

#### Representative calculation of accuracy for 2-indanone, run 1.

The ratio of AEP–2-indanone in the combined mixture  $A_{32}:B_{33}:C_{34}$  (run 1) was 5:3:1. Thus, the expected MST ratio at m/z 32, 33, and 34 is 5:3:1, respectively. The 32-34 MST intensities were measured from the mass spectrum generated by the integration of the GC signal for the AEP–2-indanone adduct and found to be 5.66, 3.17, and 1.17 ion counts (parent fragment ion normalized

to 100), respectively. Summing the total ion counts for the three MSTs gives 10.00, and dividing this value by 9 (sum of the total 2-indanone adduct ratio, 5:3:1) gives 1.11, which represents the unit ion count of one MST for 2-indanone. From this we can calculate the full, expected intensities for each MST: 5 = 5.55: 3 = 3.33: 1 = 1.11. Comparing the measured intensities to the expected intensities gives the error (| measured – expected | / expected): MST m/z 32 gave 5.66 ion counts = 1.98% error; MST m/z 33 gave 3.17 ion counts = 4.80% error; MST m/z 34 gave 1.17 ion counts = 5.40% error. This procedure was repeated for the second and third runs, and the three values obtained for each MST then were averaged to provide the value given in the table above.

Even though a majority of compounds do not generate any fragment ion in the ZMI region, certain compounds could be problematic because of their fragment ions may fall into the ZMI region and overlap with the AEP reporter ions. To remedy such interference, one could cross-label the samples. For example, assuming three samples  $s_1$ ,  $s_2$ , and  $s_3$  are first labeled as  $s_1$ -AEP 32,  $s_2$ -AEP 33, and  $s_3$ -AEP 34. In case a compound  $c_i$  generates a fragment ion with m/z = 33, the relative quantification of this compound by directly using the ratio of peak height from GC-MS spectrum will not be accurate because the reporter ion with m/z = 33 in sample  $s_2$  is interfered by the fragment ion generated by native  $c_i$ . A second experiment is needed by labeling the three samples using different AEP tags such as  $s_1$ -AEP 34,  $s_2$ -AEP 32 and  $s_3$ -AEP 33, where compound  $c_i$  is labeled with AEP 32 in sample  $s_2$ . Such a cross-label strategy enables account for any signal from non-specific interference ions.

#### **III.** Turmeric Extract Profiling and Absolute Quantification

#### A. Derivatization Procedure

Turmeric extract (steam distilled curcuma essential oil) from the roots of Curcuma Longa (India) was purchased from New Directions Aromatics Inc. (San Ramon, CA). Curcuma oil (10  $\mu$ L) was dissolved in acetonitrile (90  $\mu$ L). Equimolar quantities of AEP-33 reagent and AEP-34 reagent (2 mgs each) were dissolved in acetonitrile (100  $\mu$ L), and the mixture then was added to the curcuma oil solution. The resultant AEP reagent – curcuma oil mixture was stirred at 40 °C for 1 hour.

Analyses of the derivatized mixture were performed using a Pegasus 4D GC×GC/TOF-MS instrument (LECO Corporation, St. Joseph, MI) equipped with an Agilent 6890 gas chromatograph featuring a two-stage cryogenic modulator and secondary oven. A 60 m  $\times$  0.25 mm i.d.  $\times$  0.25 µm (film thicknesses) DB-5ms GC capillary column ((5%-phenyl)dimethylpolysiloxane, Agilent Technologies J&W) was used as the primary column for the GC×GC/TOF-MS analysis. A second GC column of 1 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m film thickness, DB-17ms ((50%-Phenyl)-methylpolysiloxane, Agilent Technologies J&W) was placed inside the secondary GC oven after the thermal modulator. The helium carrier gas flow rate was set to 2 mL/min at a corrected constant flow via pressure ramps. The inlet temperature was set at 280 °C. The primary column temperature was programmed with an initial temperature of 60 °C for 0.5 min and then ramped at 5 °C /min to 270 °C to keep 12 min. The secondary column temperature program was set to an initial temperature of 80 °C for 0.5 min and then also ramped at the same temperature gradient employed in the first column to 290 °C accordingly. The thermal modulator was set to +20 °C relative to the primary oven, and a modulation time of 2 s was used. The hot pulse time is 0.4 s. The mass range was 25-800 m/z with an acquisition

rate of 200 spectra per second. The ion source chamber was set at 230 °C with the MS transfer line temperature set to 280 °C, and the detector voltage was 1450 V with electron energy of 70 eV. The acceleration voltage was turned on after a solvent delay of 325 s. 2  $\mu$ L samples were injected into the system with a split ratio of 50:1. The GC×GC–TOF MS data were processed using LECO's instrument control software ChromaTOF for peak picking.

#### **B.** Absolute Quantification

Turmeric extract (steam distilled curcuma essential oil) from the roots of Curcuma Longa (India) was purchased from New Directions Aromatics Inc. (San Ramon, CA). Curcuma oil (10  $\mu$ L) was dissolved in acetonitrile (90  $\mu$ L). 2 mg of AEP-33 reagent were dissolved in 100  $\mu$ L of acetonitrile and added to the dissolved curcuma oil. Derivatization was carried out at 40 °C for 1 hour and followed by storing at 5 °C for 72 hours.

AEP-34 adduct of 2-nonanone (Z-isomer) and AEP-34 adduct of 2-undecanone (Z-isomer) were used as standards for the quantification experiments. Solutions of these two standards were formulated in acetonitrile at 40.6  $\mu$ g/mL (155 nmol/mL) and 16  $\mu$ g/mL (55 nmol/mL), respectively. The derivatized curcuma oil (30  $\mu$ L) was mixed with the AEP-34 adduct of 2-nonanone (Z-isomer, 7.5  $\mu$ L of a 40.6  $\mu$ g/mL solution) and the AEP-34 adduct of 2-undecanone (Z-isomer, 7.5  $\mu$ L of a 16  $\mu$ g/mL solution). Three separate 'spike-in' experiments were performed, and then each was analyzed by GCxGC-TOF-MS.

The following table summarizes the averages, calculated from three separate experiments, for the ratios of the reporter MSTs, the average concentration for each isomer of the carbonyl substrates and the total concentration of the carbonyl substrates in the sample. The

table shows the chromatogram peak area ratio of the *Z*- and *E*-isomers in the turmeric extract derivatized with AEP-33 before spike-in with the AEP-34 modified *Z*-isomers.

Carbonyl substrate	Chromatogram isomer ratio before spike-in		Average MST ratio in spike-in (Z-isomer)		Normalized average ion counts		Standard deviation		Determined injection concentration (µg/mL)		Determined injection concentration	Total concentration in the extract
	Ζ	E	33	34	33	34	33	34	Ζ	Ε	(µg/IIIL)	(µg/IIIL)
2-nonanone	1	2.07	1.05	1	18.4	17.5	1.3	0.9	7.1 (±0.4)	14.7 (±0.9)	21.8 (±1.3)	327.0 (±20)
2-undecanone	1	1.63	3.55	1	13.5	3.8	0.5	1.3	9.4 (±1)	15.4 (±1.7)	24.8 (±2.7)	372.0 (±41)

The total concentration of the AEP-33 adducts in the extract were found to be  $327.0 \pm 20 \ \mu g/mL$ (1.25  $\pm 0.08 \ \mu mol/mL$ ) for the 2-nonanone adduct, and  $372.0 \pm 41 \ \mu g/mL$  (1.28  $\pm 0.14 \ \mu mol/mL$ ) for the 2-undecanone adduct. These values correspond to  $178 \pm 14 \ \mu g/mL$  of 2-nonanone, and  $218 \pm 24 \ \mu g/mL$  of 2-undecanone, in the initial extract.

2-hydroxyphthalimide 4, <sup>1</sup>H NMR (400 MHz) CDCl<sub>3</sub>





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2-hydroxyphthalimide 4, <sup>13</sup>C NMR (100 MHz) CDCl<sub>3</sub>
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Phthalimide ester 5a, <sup>1</sup>H NMR (400 MHz) CDCl<sub>3</sub>



Phthalimide ester 5a, <sup>13</sup>C NMR (100 MHz) CDCl<sub>3</sub>



# AEP-32, <sup>1</sup>H NMR (400 MHz) CDCl<sub>3</sub>





1 1 1 ppm





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Phthalimide ester 5b, <sup>13</sup>C NMR (100 MHz) CDCl<sub>3</sub>
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# AEP-33, <sup>1</sup>H NMR (400 MHz) CDCl<sub>3</sub>



AEP-33, <sup>13</sup>C NMR (100 MHz) CDCl<sub>3</sub>



Phthalimide ester 5c, <sup>1</sup>H NMR (400 MHz) CDCl<sub>3</sub>









AEP-34, <sup>13</sup>C NMR (100 MHz) CDCl<sub>3</sub>



























