# Supporting Information for

# Base- and Metal-free Direct C–H Direct Arylations of Naphthalene and other Unbiased Arenes with Diaryliodonium Salts

Susana Castro,<sup>a</sup> Juan J. Fernández,<sup>b</sup> Rubén Vicente, \*<sup>a</sup> Francisco J. Fañanás, \*<sup>a</sup> and Félix Rodríguez\*<sup>a</sup>

<sup>a</sup> Instituto Universitario de Química Organometálica "Enrique Moles", Universidad de Oviedo, Julián Clavería 8, 33006-Oviedo (Spain).

<sup>b</sup> R&D Department, Industrial Química del Nalón S. A., Avenida de Galicia 31, 33005-Oviedo, Spain.

General remarks.	3
Screening studies of metal-free direct arylations of naphthalene.	4
IPC-MS analysis.	6
Representative procedure for metal-free direct arylations of unbiased arenes.	7
Mechanistic experiments.	13
<sup>1</sup> H-, <sup>13</sup> C-NMR spectra of pure compounds.	14
GC-MS Chromatograms and Mass spectra of compounds 2-4.	20

**General remarks.** All operations were carried out under nitrogen atmosphere using conventional Schlenck techniques. Solvents were dried according to normal procedures and used immediately after distillation. Naphthalene was provided by Industrial Química del Nalón, S. A., at highest purity available. Other arenes were purchased from Aldrich at their highest purity available and used as received. All glassware and stirring bars used in this work were new. Reactions carried out under conventional heating were performed at the indicated temperature in a pre-heated oil bath. Microwave reactions were carried out in a *Biotage Initiator+ Microwave System* apparatus and microwave vials were sealed using reseal septa. TLC analysis was performed on aluminium-backed plates coated with silica gel 60, 230-400 mesh. High-resolution mass spectra were determined on a Finnigan MAT95 spectrometer. NMR spectra were run on Bruker AV-300, AV-400, NAV-400 and AV-600 spectrometers. GC-MS analysis was performed on Agilent Technologies apparatus (6890N Network GC System, 5973 Network Mass Selective Detector).

### Screening studies of metal-free direct arylations of naphthalene.

<u>Under conventional heating</u>: Naphthalene (0.5 mmol) and diphenyliodonium triflate (0.6 mmol, 1.2 equiv) were place on a schlenk flask, sealed with a septum and subject to three cycles of vacuum/nitrogen. Solvent (2.0 mL) was added and the reaction mixture was heated in a preheated oil bath according to the conditions described in Table 1. After 72 h, the resulting mixture was cooled down, dried and the residue was analyzed by GC-MS and purified by column chromatography (hexanes, SiO<sub>2</sub>). Solvent-free reactions were performed using naphthalene in excess (5.0 equiv) with respect to diphenyliodonium triflate (0.5 mmol).

<u>Under microwave irradiation</u>: Naphthalene (2.5 mmol, 5.0 equiv.) and diphenyliodonium triflate (0.5 mmol) were place on a microwave vial, sealed with a septum and subject to three cycles of vacuum/nitrogen. This mixture was subjected to microwave irradiation at the temperature indicated in Table 1. After 30 min, the resulting mixture was cooled down and the residue was analyzed by GC-MS and purified by column chromatography (hexanes, SiO<sub>2</sub>).

	+ Pr	h <sub>2</sub> IOTf <u>Solvent</u> Conditions 1a	Ph
Entry	Solvent	Conditions <sup>a</sup>	<b>1a</b> (%) / α:β <sup>a</sup>
1	Dodecane	100°C, 72h	_b
2	Acetonitrile	85°C, 72h	_b
3	N,N-Dimethylacetamide	100°C, 72h	_b
4	Nitrobenzene	130°C, 72h	_b
5	1,4-Dioxane	105°C, 72h	24 / 5:1
6	1,2-Dichloroethane	85°C, 72h	49 / 6:1
7 <sup>c</sup>		85°C, 72h	46 / 8:1
8 <sup>c</sup>		120ºC, 72h	57 / 1.2:1
9 <sup>c</sup>		MW. 120°C. 30 min	70 / 7:1

**Table 1**. Initial screening of metal-free direct arylation of naphthalene.

<sup>a</sup> Yields of isolated product after purification by column chromatography (SiO<sub>2</sub>). The selectivity was determined by <sup>1</sup>H-NMR analysis. <sup>b</sup> **1a** was not detected by GC/MS analysis. <sup>c</sup> Naphthalene (2.5 mmol; 5 equiv), diphenyliodonium triflate (0.5 mmol).

	(n equiv)	+ Ph <sub>2</sub> IOTf <u>Co</u> r	Iditions	Ph 1a
Entry	n (equiv)	T (°C)	t (min)	<b>1a</b> (%) / α:β <sup>a</sup>
1	5	120	30	70 / 7:1
2	4	120	30	40 / 7:1
3	2.5	120	30	30 / 8:1
4	1.5	120	30	42 / 7:1
5	5	100	30	<5 / n.d.
6	5	150	30	56 / 6:1
7	5	120	15	25 / 6:1
8	5	120	20	40 / 6:1
9	5	120	45	62 / 5:1
10	5	120	60	64 / 6:1
11 <sup>b</sup>	5	120	30	29 / 6:1

Table 2. Influence of relative ratio, temperature and time.

<sup>a</sup> Yields of isolated product after purification by column chromatography (SiO<sub>2</sub>). The selectivity was determined by <sup>1</sup>H-NMR analysis. <sup>b</sup> Reaction was performed in the presence of air. (n. d. = not determined).

Table 3. Influence of the diphenyliodonium salt.

	+ Ph <sub>2</sub> IX —	MW 120 °C, 30 min 1a
Entry	Х	<b>1a</b> (%) / α:β <sup>a</sup>
1	OTf	70 / 8:1
2	Br	-
3	$BF_4$	-
4	OTs	-
5	$BF_4$	-
6	OAc	-
7	OTFAc	

<sup>a</sup> Yields of isolated product after purification by column chromatography (SiO<sub>2</sub>). The selectivity was determined by <sup>1</sup>H-NMR analysis.

#### **ICP-MS** analysis.

IPC-MS analysis were performed on a IPC-MS 7500ce apparatus. Metal concentration was determined using the ChemStation of this equipment. Samples preparation was as follows: a 70 mg sample was digested with  $HNO_3$  (30 % vol). The resulting mixture was diluted 1:10 with  $HNO_3$  (1 % vol). To this solution, solutions containing Sc, Rh, In and TI at 5 ppb were added as internal standards. The results of the analysis are given bellow:

Metal (ppm)	Ph₂lOTf	Naphthalene
В	0.66	nd
Al	0.60	nd
V	nd	nd
Cr	1.18	nd
Mn	0.02	nd
Fe	2.09	nd
Ni	0.57	nd
Cu	1.44	nd
Zn	4.07	nd
Ag	0.88	0.04
Sn	0.04	nd
Sb	0.12	nd
Ва	0.12	nd
Се	0.02	0.01
Au	0.02	nd
Pb	0.03	nd
Pd	0.02	nd
Rh	nd	nd
Ru	nd	nd

Nd: not detected

### Representative procedure for metal-free direct arylations of unbiased arenes.

#### Phenylnaphthalene 1a (Table 2, entry 1).

Naphthalene (320 mg, 2.5 mmol, 5 equiv.) and diphenyliodonium triflate (215 mg, 0.5 mmol) were place in pre-dried microwave vial with a stirring bar, sealed with a septum and subjected to three cycles of vacuum/nitrogen. The mixture was heated at 120 °C under microwave irradiation for 30 min. The resulting mixture was cooled down to ambient temperature and purified by column chromatography on silica gel (hexanes) to afford phenylnaphthalene **1a** as a mixture of regioisomers (pale beige solid, 72 mg, 70 %,  $\alpha$ : $\beta$  = 7:1, estimated by <sup>1</sup>H-NMR and GC-MS analysis). A further purification allowed the isolation of part of the major regioisomer in pure form.

1-Phenylnaphthalene: <sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.97-7.90 (m, 3H), 7.55–7.48 (m, 9H). <sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 140.8 (C<sub>q</sub>), 140.3 (C<sub>q</sub>), 133.9 (C<sub>q</sub>), 131.7 (C<sub>q</sub>), 130.1 (2 x CH), 128.3 (2 x CH), 127.7 (CH), 127.3 (CH), 127.0 (CH), 126.1 (2 x CH), 125.8 (CH), 125.4 (CH). **HR-MS** (IE) calc. for C<sub>16</sub>H<sub>12</sub> [M]<sup>+</sup> 204.0939, found 204.0950. NMR data were consistent with that reported in literature.<sup>1</sup>

#### (4-Fluorophenyl)naphthalene 1b (Table 2, entry 2).

Following the representative procedure (150 °C, 60 min), di(4-fluorophenyl)iodonium triflate (233 mg, 0.5 equiv.) was used. After purification by column chromatography (SiO<sub>2</sub>, hexanes) yielded **1b** as a mixture of regioisomers (white solid, 88 mg, 79 %,  $\alpha$ : $\beta$  = 8:1, estimated by <sup>1</sup>H-NMR and GC-MS analysis). A further purification allowed the isolation of part of the major regioisomer in pure form.

1-(4-Fluorophenyl)naphthalene: <sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.93 (d, J = 8.2 Hz, 1H), 7.87 (t, J = 8.7 Hz, 2H), 7.55–7.40 (m, 6H), 7.20 (t, J = 8.7 Hz, 2H). <sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 162.3 (d, J = 246.2 Hz, C<sub>q</sub>), 139.2 (C<sub>q</sub>), 136.6 (d, J = 3.5 Hz, C<sub>q</sub>), 133.8 (C<sub>q</sub>), 131.6

<sup>&</sup>lt;sup>1</sup> L. Wang and W. Lu, *Org. Lett.*, 2009, **11**, 1079.

(C<sub>q</sub>), 131.5 (d, *J* = 7.9 Hz, 2 x CH), 128.3 (CH), 127.8 (CH), 127.0 (CH), 126.2 (CH), 125.8 (CH), 125.7 (CH), 125.3 (CH), 115.2 (d, *J* = 21.3 Hz, 2 x CH). <sup>19</sup>**F-NMR** (282 MHz, CDCl<sub>3</sub>):  $\delta$  = –115.5 (s). **HR-MS** (IE) calc. for C<sub>16</sub>H<sub>11</sub>F [M]<sup>+</sup> 222.0845, found 222.0860. NMR data were consistent with that reported in literature.<sup>2</sup>

### (4-Chlorophenyl)naphthalene 1c (Table 2, entry 3).

Following the representative procedure (150 °C, 60 min), di(4-chlorophenyl)iodonium triflate (294 mg, 0.5 equiv.) was used. After purification by column chromatography (SiO<sub>2</sub>, hexanes) yielded **1c** as a mixture of regioisomers (pale yellow oil, 70 mg, 59 %,  $\alpha$ : $\beta$  = 5:1, estimated by <sup>1</sup>H-NMR and GC-MS analysis). A further purification allowed the isolation of part of the major regioisomer in pure form.

1-(4-Chlorophenyl)naphthalene: <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.93 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.56–7.30 (m, 8H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 139.2 (C<sub>q</sub>), 139.0 (C<sub>q</sub>), 133.8 (C<sub>q</sub>), 133.3 (C<sub>q</sub>), 131.5 (C<sub>q</sub>), 131.4 (2 x CH), 128.5 (2 x CH), 128.4 (CH), 128.0 (CH), 126.9 (CH), 126.3 (CH), 125.9 (CH), 125.7 (CH), 125.4 (CH). HR-MS (IE) calc. for C<sub>16</sub>H<sub>11</sub>Cl [M]<sup>+</sup> 238.0549, found 238.0558. NMR data were consistent with that reported in literature.<sup>3</sup>

### (4-Bromophenyl)naphthalene 1d (Table 2, entry 4).

Following the representative procedure (150 °C, 60 min), di(4-bromophenyl)iodonium triflate (249 mg, 0.5 equiv.) was used. After purification by column chromatography (SiO<sub>2</sub>, hexanes) yielded **1d** as a mixture of regioisomers (pale yellow oil, 98 mg, 69 %,  $\alpha$ : $\beta$  = 3:1, estimated by

<sup>&</sup>lt;sup>2</sup> K. W. Quasdorf, A. Antoft-Finch, P. Liu, A. L. Silberstein, A. Komaromi, T. Blackburn, S. D. Ramgren, K. N. Houk, V. Snieckus and N. K. Garg, *J. Am. Chem. Soc.*, 2011, **133**, 6352.

<sup>&</sup>lt;sup>3</sup> A. C. Glass, B. B. Morris, L. N. Zakharov and S.-Y. Liu, Org. Lett., 2008, **10**, 4855.

<sup>1</sup>H-NMR and GC-MS analysis). A further purification allowed the isolation of part of the major regioisomer in pure form.

1-(4-Bromophenyl)naphthalene: <sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.93 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.55–7.50 (m, 2H), 7.46 (dt, *J* = 6.8, 1.2 Hz, 1H), 7.42–7.38 (m, 3H). <sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 139.7 (C<sub>q</sub>), 138.9 (C<sub>q</sub>), 133.8 (C<sub>q</sub>), 131.7 (2 x CH), 131.5 (2 x CH), 131.4 (C<sub>q</sub>), 128.4 (CH), 128.0 (CH), 126.9 (CH), 126.3 (CH), 125.9 (CH), 125.7 (CH), 125.4 (CH), 121.5 (C<sub>q</sub>). **HR-MS** (IE) calc. for C<sub>16</sub>H<sub>11</sub>Br [M]<sup>+</sup> 282.0044, found 282.0061. NMR data were consistent with that reported in literature.<sup>1</sup>

#### (4-Tolyl)naphthalene 1e (Table 2, entry 5).

Following the representative procedure (150 °C, 60 min), di(4-tolyl)iodonium triflate (229 mg, 0.5 equiv.) was used. After purification by column chromatography (SiO<sub>2</sub>, hexanes) yielded **1e** as a mixture of regioisomers (pale yellow oil, 83 mg, 76 %,  $\alpha$ : $\beta$  = 4:1, estimated by <sup>1</sup>H-NMR and GC-MS analysis). A further purification allowed the isolation of part of the major regioisomer in pure form.

1-(4-Tolyl)naphthalene: <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.93 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.55–7.45 (m, 3H), 7.44–7.39 (m, 3H), 7.32 (d, *J* = 8.0, 2H), 2.47 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 140.3 (C<sub>q</sub>), 137.8 (C<sub>q</sub>), 136.8 (C<sub>q</sub>), 133.8 (C<sub>q</sub>), 131.7 (C<sub>q</sub>), 130.0 (2 x CH), 129.0 (2 x CH), 128.2 (CH), 127.4 (CH), 126.9 (CH), 126.1 (CH), 125.9 (CH), 125.7 (CH), 125.4 (CH), 21.2 (CH<sub>3</sub>). **HR-MS** (IE) calc. for C<sub>17</sub>H<sub>14</sub> [M]<sup>+</sup> 218.1096, found 218.1106. NMR data were consistent with that reported in literature.<sup>4</sup>

<sup>&</sup>lt;sup>4</sup> G. S. Viswanathan, M. Wang and C.-J. Li, *Angew. Chem. Int. Ed.*, 2002, **41**, 2138.

### (4-tert-Butylphenyl)naphthalene 1f (Table 2, entry 6).

Following the representative procedure (150 °C, 60 min), di(4-*tert*-butyl)iodonium triflate (271 mg, 0.5 equiv.) was used. After purification by column chromatography (SiO<sub>2</sub>, hexanes) yielded **1f** as a mixture of regioisomers (pale yellow oil, 96 mg, 74 %,  $\alpha$ : $\beta$  = 10:1, estimated by <sup>1</sup>H-NMR and GC-MS analysis). A further purification allowed the isolation of part of the major regioisomer in pure form.

1-(4-*tert*-Butylphenyl)naphthalene: <sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.97 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.54–7.43 (m, 8H), 1.42 (s, 9H). <sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.1 (C<sub>q</sub>), 140.2 (C<sub>q</sub>), 137.7 (C<sub>q</sub>), 133.8 (C<sub>q</sub>), 131.7 (C<sub>q</sub>), 129.7 (2 x CH), 128.2 (CH), 127.4 (CH), 126.9 (CH), 126.2 (CH), 125.9 (CH), 125.7 (CH), 125.4 (CH), 125.2 (2 x CH), 34.6 (C<sub>q</sub>), 31.5 (3 x CH<sub>3</sub>). **HR-MS** (IE) calc. for C<sub>20</sub>H<sub>20</sub> [M]<sup>+</sup> 260.1565, found 260.1577.<sup>5</sup>

#### Phenylphenanthrene 2a (Table 3).

Following the representative procedure, phenanthrene (445 mg, 2.5 mmol, 5.0 equiv.) and diphenyliodonium triflate (215 mg, 0.50 mmol) were used. After heating 1 h at 150 °C under microwave irradiation and purification by column chromatography on (SiO<sub>2</sub>, hexanes), yielded **2a** as a mixture of regioisomers (pale beige solid, 70 mg, 55 %, 8.4:1.2:1.1:1, estimated by GC-MS analysis).<sup>6</sup>

### (4-Tolyl)phenanthrene 2b (Table 3).

Following the representative procedure, phenanthrene (445 mg, 2.5 mmol, 5.0 equiv.) and di(4-tolyl)iodonium triflate (229 mg, 0.50 mmol) were used. After heating 1 h at 150 °C under microwave irradiation and purification by column chromatography on (SiO<sub>2</sub>, hexanes), yielded

<sup>&</sup>lt;sup>5</sup> B. Sreedhar, D. Yada, P. S. Reddy, *Adv. Synth. Catal.*, 2011, **353**, 2823.

<sup>&</sup>lt;sup>6</sup> The GC-MS estimation given refers to the peaks found on the chromatogram. Since 5 regioisomers could be obtained, it is likely that some peaks corresponding to different regioisomers appeared overlapped in the chromatogram.

**2b** as a mixture of regioisomers (pale beige solid, 73 mg, 54 %, 12:4:1, estimated by GC and GC-MS analysis).<sup>7</sup>

### Phenyl-2,6-Dimethylnaphthalene 3 (Table 3).

Following the representative procedure, 2,6-dimethylnaphthalene (391 mg, 2.5 mmol, 5.0 equiv.) and diphenyliodonium triflate (215 mg, 0.50 mmol) were used. After heating 1 h at 150 °C under microwave irradiation and purification by column chromatography on (SiO<sub>2</sub>, hexanes), yielded **5** as a mixture of regioisomers (pale beige solid, 53 mg, 47 %, 16:12:1), estimated by GC-MS analysis).

## Phenylpyrene 4a (Table 3).

Following the representative procedure, pyrene (505 mg, 2.5 mmol, 5.0 equiv.) and diphenyliodonium triflate (215 mg, 0.5 mmol) were used. After heating 30 min at 160 °C under microwave irradiation and purification by column chromatography on (SiO<sub>2</sub>, hexanes), yielded **4a** as a mixture of regioisomers (pale beige solid, 100 mg, 72 %, 2.3:1.5:1, estimated by GC-MS analysis).

# (4-Tolyl)pyrene 4b (Table 3).

Following the representative procedure, pyrene (162 mg, 0.8 mmol, 5.0 equiv.) and di(4-tolyl)iodonium triflate (73 mg, 0.16 mmol) were used. After heating 30 min at 160 °C under microwave irradiation and purification by column chromatography on (SiO<sub>2</sub>, hexanes), yielded

<sup>&</sup>lt;sup>7</sup> The GC-MS estimation given refers to the peaks found on the chromatogram. Since 5 regioisomers could be obtained, it is likely that some peaks corresponding to different regioisomers appeared overlapped in the chromatogram.

**4b** as a mixture of regioisomers (pale beige solid, 40 mg, 85 %, 2.6:1, estimated by GC-MS analysis).<sup>8</sup>

<sup>&</sup>lt;sup>8</sup> The GC-MS estimation given refers to the peaks found on the chromatogram. Since 3 regioisomers could be obtained, it is likely that some peaks corresponding to different regioisomers appeared overlapped in the chromatogram.

### Mechanistic experiments (Scheme 2).

In the presence of a radical scavenger: Naphthalene (320 mg, 2.5 mmol, 5 equiv.), diphenyliodonium triflate (215 mg, 0.5 mmol) and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) (78 mg, 0.5 mmol, 1.0 equiv.) were place in pre-dried microwave vial with a stirring bar, sealed with a septum and subjected to three cycles of vacuum/nitrogen. The mixture was heated at 120 °C under microwave irradiation for 30 min. The resulting mixture was cooled down to ambient temperature and no arylation products were detected by <sup>1</sup>H-NMR and GC-MS analysis.

In the presence of triflic acid: Naphthalene (320 mg, 2.5 mmol, 5 equiv.), diphenyliodonium bromide (180 mg, 0.5 mmol) and triflic acid (44  $\mu$ L, 0.5 mmol, 1.0 equiv.) were place in pre-dried microwave vial with a stirring bar, sealed with a septum and subjected to three cycles of vacuum/nitrogen. The mixture was heated at 120 °C under microwave irradiation for 30 min. The resulting mixture was cooled down to ambient temperature and no arylation products were detected by <sup>1</sup>H-NMR and GC-MS analysis.







ò 110 100 f1 (ppm) 







110 100 f1 (ppm) ò 







```
File
               :D:\datos\Joaquin\SU475.D
Operator
               :
               : 24 Apr 2012 19:46
                                               using AcgMethod ALBA INYECTOR = 250
Acquired
Instrument :
                      masas
Sample Name: SU475
Misc Info :
Vial Number: 27
                                                     TIC: SU475.D
    Abundance
8000000
                                                                                    17.25
     7000000
     6000000
                                                       Ph
      5000000
      4000000
                                            2a
     3000000
     2000000
                                                                                    17.32
      1000000
                                                                                      17.87
                                                                                16.57
             3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00
    Time-->
   Integration Parameters: autointl.e
   Integrator: ChemStation
   Smoothing : OFF
                                                         Filtering: 5
                                                          Min Area: 5 % of largest Peak
   Sampling : 1
   Start Thrs: 0.2
                                                        Max Peaks: 100
   Stop Thrs : 0
                                                    Peak Location: TOP
   If leading or trailing edge < 100 prefer < Baseline drop else tangent > % \left( \left( {{{\left( {{{\left( {{{\left( {{{\left( {{{c}}} \right)}} \right.} \right.} \right)}_{0,0}}}} \right)} \right)
   Peak separation: 5
   Method
            : C:\MSDCHEM\1\METHODS\REPOSO.M
   Title
              : borrar
   Signal
            : TIC
 peak R.T. first max last PK
# min scan scan scan TY
                                          peak
                                                       corr.
                                                                 corr.
                                                                             % of
                                         height
                                                       area
                                                                  % max.
                                                                            total
                                          -----
   1 16.571 2321 2327 2337 BB
                                           764790
                                                    12707030
                                                                11.95%
                                                                             8.503%
               2428 2437 2444 BV
2444 2450 2464 PV
2532 2538 2554 BB
                                                                            71.179%
                                          7221899 106372981 100.00%
   2
      17.247
                                          1266852 15885510 14.93% 10.630%
797316 14479815 13.61% 9.689%
   3
      17.327
      17.867
   4
                              Sum of corrected areas: 149445336
```

REPOSO.M Thu Apr 26 13:52:05 2012





Chemical Formula:  $C_{20}H_{14}$ Exact Mass: 254,11 Molecular Weight: 254,33 m/z: 254.11 (100.0%), 255.11 (21.6%), 256.12 (2.3%)

#### Electronic Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2012

```
File
              :D:\datos\Joaquin\SU476.D
Operator
Acquired
              : 24 Apr 2012 20:19
                                              using AcqMethod ALBA INYECTOR = 250
Instrument :
                    masas
Sample Name: SU476
Misc Info :
Vial Number: 28
                                                  TIC: SU476.D
    Abundance
6000000
                                                                                  17 86
     5500000
     5000000
                                                    Me
     4500000
     4000000
     3500000
     3000000
                                                                              17,11
     2500000
                                  2b
     2000000
     1500000
     1000000
                                                                                  17.93
     500000
    Time-->
           3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00
   Integration Parameters: autoint1.e
   Integrator: ChemStation
   Smoothing : OFF
                                                     Filtering: 5
Min Area: 5 % of largest Peak
Max Peaks: 100
   Sampling : 1
  Start Thrs: 0.2
Stop Thrs : 0
                                                 Peak Location: TOP
   If leading or trailing edge < 100 prefer < Baseline drop else tangent > % \left( \left( {{{\left( {{{\left( {{{\left( {{{\left( {{{c}}} \right)}} \right.} \right.} \right)}_{0,0}}}} \right)} \right)
  Peak separation: 5
            : C:\MSDCHEM\1\METHODS\REPOSO.M
  Method
  Title
             : borrar
  Signal : TIC
 peak R.T. first max last PK
                                       peak
                                                    corr.
                                                                        % of
                                                              corr.
   # min
              scan scan scan TY
                                      height
                                                    area
                                                             % max.
                                                                        total
      -----
                     -----
                           ---- ---
                                       -----
                                                   -----
                                                                       _____
     17.106
              2404 2414 2431 BV
                                       2408329
                                                  30663211 33.56%
                                                                       23.611%
              2528 2538 2543 BV
2543 2548 2563 PB
  2
     17.867
                                       5908413
                                                  91376473 100.00%
                                                                       70.362%
     17.929
                                                              8.57%
                                        490576
                                                   7826532
                                                                        6.027%
                            Sum of corrected areas: 129866216
REPOSO.M Thu Apr 26 13:52:46 2012
```





Chemical Formula: C<sub>21</sub>H<sub>16</sub> Exact Mass: 268,13 Molecular Weight: 268,35 m/z: 268.13 (100.0%), 269.13 (22.9%), 270.13 (2.5%)

```
File
             :D:\datos\Joaquin\SU474.D
Operator
Acquired
             : 24 Apr 2012 19:14
                                            using AcqMethod ALBA INYECTOR = 250
Instrument :
                   masas
Sample Name: SU474
Misc Info :
Vial Number: 26
    Abundance
                                              TIC: SU474.D
                                                              14 66
     1.4e+07
                                                                15.07
     1.3e+07
     1.2e+07
     1.1e+07
                                  Ph
      1e+07
                                           Me
     9000000
     8000000
                       Me
     7000000
                                   3
    6000000
    5000000
     4000000
    3000000
    2000000
                                                             14.47
    1000000
   Time-->
            3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00
                             Area Percent Report
 Data Path : D:\datos\Joaquin\
Data File : SU474.D
  Acq On
            : 24 Apr 2012 19:14
 Operator
 Sample
            : SU474
 Misc
 ALS Vial : 26 Sample Multiplier: 1
 Integration Parameters: autointl.e
 Integrator: ChemStation
 Smoothing : OFF
                                                Filtering: 5
 Sampling : 1
                                                  Min Area: 5 % of largest Peak
 Start Thrs: 0.2
                                                Max Peaks: 100
 Stop Thrs : 0
                                            Peak Location: TOP
 If leading or trailing edge < 100 prefer < Baseline drop else tangent >
 Peak separation: 5
 Method
           : C:\MSDCHEM\1\METHODS\REPOSO.M
 Title
           : borrar
 Signal
          : TIC
peak R.T. first max last PK
                                    peak
                                               corr.
                                                        corr.
                                                                  % of
 # min
            scan scan scan
                              ΤY
                                  height
                                              area
                                                        8 max.
                                                                 total
                       ---- ---
                  ----
                                   -----
                                                        -----
                                                                 ____.
1
2
   14.471
           1975 1985 1995 BB
                                   1447703 16630953
                                                         5.89%
                                                                  3.317%
                                  15327231 282333118 100.00% 56.304%
12135104 202477313 71.72% 40.379%
   14.667
            2002 2017 2025 BB
   15.067
            2068 2082 2094 BB
```





Chemical Formula: C<sub>18</sub>H<sub>16</sub> Exact Mass: 232,13 Molecular Weight: 232,32 m/z: 232.13 (100.0%), 233.13 (19.7%), 234.13 (1.8%)

```
File :D:\datos\Joaquin\SU500.D
Operator :
Acquired : 25 Apr 2012 10:54 using AcqMethod ALBA INYECTOR = 250
Instrument : masas
Sample Name: SU500
Misc Info :
Vial Number: 30
```



Sum of corrected areas: 852396809

REPOSO.M Thu Apr 26 13:47:38 2012





4a

Chemical Formula:  $C_{22}H_{14}$ Exact Mass: 278,11 Molecular Weight: 278,35 m/z: 278.11 (100.0%), 279.11 (23.8%), 280.12 (2.7%)

```
File
             :D:\datos\Joaquin\SU477.D
Operator
             1
Acquired
             : 25 Apr 2012 10:20 using AcqMethod ALBA INYECTOR = 250
Instrument :
                   masas
Sample Name: SU477
Misc Info :
Vial Number: 29
   Abundance
                                                TIC: SU477.D
                                                                                       19 75
     4500000
                                                   Me
     4000000
     3500000
    3000000
    2500000
                                                                                      19.64
    2000000
                                    4b
     1500000
     1000000
     500000
   Time--> 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00
  Integration Parameters: autointl.e
  Integrator: ChemStation
                                                   Filtering: 5
Min Area: 5 % of largest Peak
Max Peaks: 100
  Smoothing : OFF
  Sampling : 1
  Start Thrs: 0.2
  Stop Thrs : 0
                                               Peak Location: TOP
  If leading or trailing edge < 100 prefer < Baseline drop else tangent >
  Peak separation: 5
           : C:\MSDCHEM\1\METHODS\REPOSO.M
: borrar
  Method
  Title
  Signal : TIC
 peak R.T. first max last PK peak
# min scan scan scan TY height
                                                corr.
                                                                     % of
                                                           corr.
                                                area % max. total
                                     _____
  1 19.642 2819 2827 2836 PV 2165245 26113638 39.25% 28.188%
2 19.753 2836 2845 2866 VV 4329189 66527110 100.00% 71.812%
                           Sum of corrected areas: 92640748
```

REPOSO.M Thu Apr 26 13:45:47 2012





Chemical Formula: C<sub>23</sub>H<sub>16</sub> Exact Mass: 292,13 Molecular Weight: 292,37 m/z: 292.13 (100.0%), 293.13 (25.1%), 294.13 (3.0%)