Synthesis of terminal arylacetylenes by a Stille coupling reaction catalysed by a MCM-41-supported bidentate phosphine palladium(0) complex

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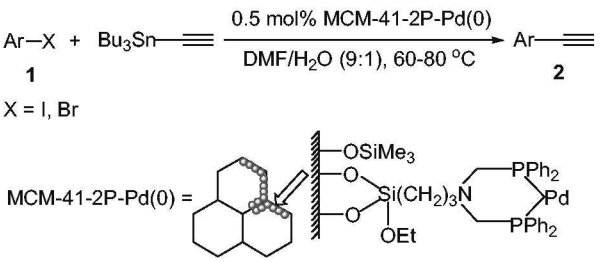
A variety of terminal arylacetylenes have been conveniently synthesised in good to high yields by Stille coupling of aryl halides with ethynyltributylstannane catalysed by a MCM-41-supported bidentate phosphine palladium(0) complex in an aqueous medium and under air. Our system not only avoids the requirement for water-free and oxygen-free conditions, but also solves the basic problem of palladium catalyst reuse.

Keywords: Stille coupling, MCM-41-supported catalyst, bidentate phosphine palladium complex, heterogeneous catalysis

Terminal arylacetylenes are important synthetic intermediates[1-5] and are usually prepared by classical methods such as the Vilsmeier method,[6,7] the halogenation–dehydrohalogenation sequence of vinyl aromatics[8] and ketones,[9,10] and the dehydrohalogenation of β,β-dihaloolefins.[11,12] However, these methods involve tedious multistep synthetic procedures and the yields are poor to moderate. The synthesis of terminal arylacetylenes by the Sonogashira reaction requires (a) preparation of monoprotected ethynes, such as $Me_3SiC{\equiv}CH$ and $HOMe_2CC{\equiv}CH$, (b) their Sonogashira coupling[13] and (c) deprotection.[14-16] These three-step procedures are at best circuitous often leading to modest overall yields of the desired terminal arylacetylenes. The palladium-catalysed cross-coupling of organostannanes with organic halides and triflates is known as the Stille reaction[17-19] and has become an extremely powerful tool for the formation of carbon–carbon bonds. This coupling reaction has been widely applied in organic synthesis since a wide variety of functionality can be tolerated on either partner, the yields of coupled products are high and the organotin reagents can be readily synthesised, purified and stored. Ley *et al.*[20] reported that terminal arylacetylenes could be conveniently synthesised in good yields by palladium(0)-catalysed Stille coupling of aryl halides with ethynyltributylstannane. However, the limitations of the Stille reaction are the forcing conditions typically at reflux in THF or benzene and the requirement for dry and oxygen-free environments. The reaction generally proceeds in the presence of a homogeneous palladium catalyst, which makes catalyst recovery a tedious operation and might result in unacceptable palladium contamination of the product. In view of this the use of a heterogeneous palladium catalyst would be desirable.[21-24] So far, polymer-supported palladium catalysts have successfully been used for example for the Heck reaction,[25-29] the Suzuki reaction[30-35] and the Sonogashira reaction.[36-40] However, to the best of our knowledge, the Stille reaction catalysed by polymer-supported palladium complexes has received less attention[41,42] and no report of the Stille coupling of aryl halides with ethynyltributylstannane has been made using supported palladium catalysts.

Recent developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilisation of homogeneous catalysts.[43] MCM-41 has a regular pore diameter of *ca* 5 nm and a specific surface area > 700 $m^2\ g^{-1}$.[44] Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach to the surface of the channel.[45-47] Recently, we have reported the synthesis of the first MCM-41-supported bidentate phosphine palladium(0) complex [abbreviated as MCM-41-2P-Pd(0)] and found that this complex is a highly active and recyclable catalyst for the Sonogashira reaction of aryl iodides.[40] We report here that



Scheme 1

a variety of terminal arylacetylenes could be conveniently synthesised in good to high yields by Stille coupling of aryl halides with ethynyltributylstannane catalysed by MCM-41-2P-Pd(0) under aqueous and aerobic conditions (Scheme 1).

The MCM-41-supported bidentate phosphine palladium(0) complex [MCM-41-2P- Pd(0)] was prepared by our previous procedure.[40] The phosphine and palladium contents were 1.15 and 0.52 $mmol^{-1}$ g, respectively. Initially, to determine the optimum conditions, the coupling reaction of iodobenzene with ethynyltributylstannane was examined in different solvents under aerobic conditions and it was found that DMF/H_2O (9:1) was the best choice as a solvent. The results are shown in Table 1. The use of DMF, NMP and HMPA gave good yields (81–84%) and the use of THF, PhH, and CH_3CN gave lower yields (18–33%). Running the reaction in DMF/H_2O (9:1) at 60 °C for 6 h gave the coupled product **2a** in 85% yield. The same reaction at room temperature for 6 h gave the coupled product **2a** in 31% yield. Increasing the amount of palladium catalyst could shorten the reaction time but did not increase the yield of phenylacetylene (entry 10). The low palladium concentration usually led to a long period of reaction, which was consistent with our experimental result (entry 11). Taken together, good results were obtained when the coupling reaction was carried out with 0.5 mol% of MCM-41-2P-Pd(0) in DMF/H_2O (9:1) at 60 °C under aerobic conditions.

The results of MCM-41-2P-Pd(0)-catalysed cross-coupling of a variety of aryl halides with ethynyltributylstannane are summarised in Table 2. As shown the coupling reaction of aryl iodides having electron-withdrawing or electron-donating substituents with ethynyltributylstannane proceeded smoothly at 60 °C in DMF/H_2O (9:1) under aerobic conditions giving the corresponding terminal arylacetylenes in high yields after 6 h. The substituent effects in the aryl iodides appeared to be less significant than in the aryl bromides and the reactivity of aryl bromides with electron-withdrawing substituents was higher than that of aryl bromides with electron-donating substituents. The coupling reactions of aryl bromides with ethynyltributylstannane at 60 °C gave the corresponding terminal arylacetylenes in moderate yields after 18–24 h. However, the same reactions

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Table 1 Stille coupling of iodobenzene with ethynyltributylstannane under various reaction conditions[a]

Entry	Solvent	MCM-41-2P-Pd(0)/mol%	Temp/°C	Time/h	Yield[b]/%
1	DMF	0.5	60	6	84
2	NMP	0.5	60	6	81
3	HMPA	0.5	60	6	83
4	THF	0.5	60	6	24
5	PhH	0.5	60	6	18
6	CH_3CN	0.5	60	6	33
7	DMF/H_2O (9:1)	0.5	60	6	85
8	DMF/H_2O (9:1)	0.5	25	6	31
9	DMF/H_2O (9:1)	0.5	30	18	62
10	DMF/H_2O (9:1)	1.0	60	4	83
11	DMF/H_2O (9:1)	0.2	60	24	84

[a]All reactions were performed using 1.0 mmol of iodobenzene, 1.1 mmol of ethynyltributylstannane in 2 ml of solvent under aerobic conditions.
[b]Isolated yield based on the iodobenzene used.

at 80 °C for 10–13 h gave the corresponding coupled products in good yields (entries 16–19). The Stille coupling of 1-iodonaphthalene with ethynyltributylstannane also proceeded smoothly under the same conditions affording 1-ethynylnaphthalene in 82% yield (entry 20). The optimised catalyst system is quite general and tolerant of a wide range of functional groups such as nitro, cyano, halogen, methoxy, carbonyl and hydroxy. The cross-coupling reaction of 4-bromoiodobenzene with ethynyltributylstannane afforded selectively 4-bromophenylacetylene **2b** in 87% yield; no 1,4-diethynylbenzene was formed (entry 2). In all reactions, only 0.5 mol% of MCM-41-2P-Pd(0) based on the aryl halides was used, the molar turnover numbers (TON) were much larger than those in the corresponding coupling reaction catalysed by the homogeneous palladium catalyst.[17-19]

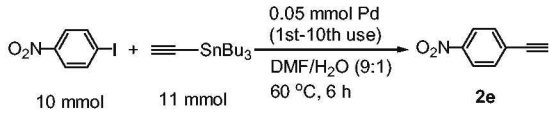
The MCM-41-supported bidentate phosphine palladium(0) catalyst can be easily recovered by simple filtration. We next examined the reuse of the catalyst by studying the Stille coupling of 4-nitroiodobenzene with ethynyltributylstannane. In general, the continuous recycle of resin-supported palladium catalysts is difficult owing to leaching of the palladium species from the polymer supports. Kang *et al.*[41] reported that the activity of a silica-supported sulfur palladium complex in the Stille coupling of aryl iodides with organostannanes decreased gradually with repeated use. However, when the coupling reaction of 4-nitroiodobenzene with ethynyltributylstannane was run even with 0.5 mol% of MCM-41-2P-Pd(0), the catalyst could be recycled 10 times without any loss of activity. The reaction promoted by the 10 th recycled catalyst afforded **2e** in 87% yield (Table 3,

Table 2 Synthesis of terminal arylacetylenes[a]

Entry	Ar–X	Temp/°C	Time/h	Product	Yield[b]/%
1	Ph–I	60	6	**2a**	85
2	4-BrC_6H_4–I	60	6	**2b**	87
3	4-ClC_6H_4–I	60	6	**2c**	84
4	4-$MeOC_6H_4$–I	60	6	**2d**	86
5	4-$O_2NC_6H_4$–I	60	6	**2e**	89
6	4-MeC_6H_4–I	60	6	**2f**	83
7	4-HOC_6H_4–I	60	6	**2g**	85
8	4-$MeCOC_6H_4$–I	60	6	**2h**	87
9	4-$MeOCOC_6H_4$–I	60	6	**2i**	84
10	3-$O_2NC_6H_4$–I	60	6	**2j**	88
11	3-MeC_6H_4–I	60	6	**2k**	85
12	3-NCC_6H_4–I	60	6	**2l**	86
13	Ph–Br	60	20	**2a**	54
14	4-ClC_6H_4–Br	60	18	**2c**	66
15	4-$MeOC_6H_4$–Br	60	24	**2d**	48
16	4-ClC_6H_4–Br	80	10	**2c**	83
17	4-$MeOC_6H_4$–Br	80	13	**2d**	77
18	4-$O_2NC_6H_4$–Br	80	10	**2e**	85
19	Ph–Br	80	12	**2a**	80
20	1-Iodonaphthalene	60	10	**2m**	82

[a]The reactions were run with 1.0 mmol of aryl halide, 1.1 mmol of ethynyltributylstannane and 0.005 mmol of the palladium catalyst in 2 ml of DMF/H_2O (9:1) under aerobic conditions.
[b]Isolated yield based on the aryl halide **1** used.

Table 3 Stille coupling of 4-nitroiodobenzene with ethynyltributylstannane catalysed by recycled catalyst



Entry	Catalyst cycle	Isolated yield/%	TON
1	First	89	178
2	Tenth	87	174
3	First to tenth consecutive	88	Total of 1760

entry 2). The average yield of **2e** in consecutive reactions promoted by the 1–10 times recycled catalyst was 88% (entry 3). The result is important from a practical point of view.

In conclusion, we have developed an efficient and direct route of synthesis of terminal arylacetylenes by the Stille coupling of aryl halides with ethynyltributylstannane catalysed by a MCM-41-supported bidentate phosphine palladium(0) complex. Because ethynyltributylstannane can be easily prepared in high yield under mild conditions from acetylene and chlorotributylstannane according to the procedure developed by Brandsma and Verkruijsse,[48] the present method has the advantages of readily available starting materials, straightforward and simple procedures, reaction in an aqueous medium and under air high yields, tolerance for a wide variety of functionality and excellent reusability of the palladium catalyst.

Experimental

^{1}H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer using $CDCl_3$ as the solvent. IR spectra were determined on an FTS-185 instrument as neat films. Mass spectra were obtained on a Finnigan 8239 mass spectrometer (EI). Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyser.

Preparation of MCM-41-NH_2

A solution of γ-aminopropyltriethoxysilane (2.20 g, 10 mmol) in dry chloroform (18 ml) was added to a suspension of the mesoporous support MCM-41 (2.80 g) in dry toluene (180 ml). The mixture was stirred for 48 h at 100 °C. Then the solid was filtered, washed by $CHCl_3$ (2 × 20 ml) and dried under reduced pressure at 160 °C for 5 h. The dried white solid was then soaked in a solution of Me_3SiCl (4.36 g, 40 mmol) in dry toluene (150 ml) at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone (3 × 20 ml) and diethyl ether (3 × 20 ml) and dried under reduced pressure at 120 °C for 5 h to obtain 3.54 g of hybrid material MCM-41-NH_2. The nitrogen content was found to be 1.27 mmol/g by elemental analysis.

Preparation of MCM-41-2P

A Schlenk flask was charged with paraformaldehyde (0.701 g, 23.3 mmol), dry MeOH (20 ml) and diphenylphosphine (4.340 g, 23.3 mmol). The reaction mixture was heated to 60 °C under Ar until the white suspension formed a colourless solution. After removal of MeOH under reduced pressure the remaining viscous oil was diluted in dry toluene (20 ml). This solution was added to a suspension of MCM-41-NH_2 (3.020 g) in dry toluene (60 ml) and the reaction mixture was heated to 105 °C under Ar for 24 h. In the cooler regions of the flask the water-toluene azeotrope separated indicating the reaction progress. After cooling to room temperature the solid product was collected by filtration under Ar, washed with dry toluene (4 × 30 ml), CH_2Cl_2/THF (1/1) (2 × 30 ml), CH_2Cl_2 (2 × 30 ml) and dried under reduced pressure (100 °C) for 5 h to give 4.08 g of the light yellow MCM-41-2P. The nitrogen and phosphine contents were found to be 0.76 mmol^{-1} g and 1.44 mmol^{-1} g, respectively.

Preparation of MCM-41-2P-Pd(0) complex

To a solution of $PdCl_2$ (0.216 g, 1.22 mmol) in acetone (50 ml) was added the MCM-41-2P (2.01 g). The reaction mixture was refluxed under Ar for 72 h. The product was allowed to cool and then filtered. The yellow solid was washed with distilled water (3 × 30 ml) and acetone (3 × 30 ml) and then stirred with hydrazine hydrate (1.6 g) and EtOH (25 ml) at 30 °C under Ar for 5 h. The resulting product was filtered, washed with EtOH (3 × 25 ml) and Et_2O (3 × 25 ml) and dried under vacuum at 60 °C to give 1.93 g of the brown MCM-41-2P-Pd(0). The nitrogen, phosphine, and palladium contents were 0.58, 1.15 and 0.52 mmol^{-1} g, respectively.

General procedure for the synthesis of terminal arylacetylenes **2a–m**

To a stirred solution of aryl iodide **1** (1.0 mmol) in DMF/H_2O (9:1) (2 ml) was added MCM-41-2P-Pd(0) (10 mg, 0.005 mmol Pd) and ethynyltributylstannane (347 mg, 1.1 mmol). The reaction mixture was stirred at 60 °C for 6 h, cooled to room temperature and diluted with diethyl ether (30 ml). The MCM-41-2P-Pd(0) was separated from the mixture by filtration, washed with distilled water (2 × 10 ml), ethanol (2 × 10 ml) and diethyl ether (2 × 10 ml) and reused in the next run. The ethereal solution was washed with saturated KF solution (10 ml) and water (2 × 10 ml) and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by SiO_2 column chromatography (light petroleum:ethyl acetate = 2:1 for **2g**; light petroleum for **2a, 2b, 2c, 2f, 2k, 2m**; light petroleum: ethyl acetate = 9:1 for **2d, 2e, 2h, 2i, 2j, 2l**).

Phenylacetylene[49] **(2a):** Colourless oil. ^{1}H NMR ($CDCl_3$): δ 7.51–7.48 (m, 2H), 7.35–7.32 (m, 3H), 3.08 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 132.1, 128.8, 128.3, 122.1, 83.7, 77.1; IR (film): ν (cm^{-1}) 3292, 2110, 1598, 1574, 1488, 757, 691; MS: *m/z* 102 (M^+, 43), 77 (65), 57 (100).

4-Bromophenylacetylene[50] **(2b):** Colourless oil. ^{1}H NMR ($CDCl_3$): δ 7.46 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 3.12 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 133.6, 131.6, 123.1, 121.1, 82.6, 78.3; IR (film): ν (cm^{-1}) 3287, 2346, 1583, 1489, 1462, 758; MS: *m/z* 181 (M^+, 1.6), 156 (38), 101 (49), 71 (60), 57 (100).

4-Chlorophenylacetylene[51] **(2c):** Colourless oil. ^{1}H NMR ($CDCl_3$): δ 7.42 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 3.10 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 134.9, 133.4, 128.7, 120.6, 82.5, 78.2; IR (film): ν (cm^{-1}) 3293, 2197, 1587, 1485, 1095, 822; MS: *m/z* 136 (M^+, 100), 135 (88), 111 (59), 69 (46).

4-Methoxyphenylacetylene[52] **(2d):** Colourless oil. ^{1}H NMR ($CDCl_3$): δ 7.42 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 3.00 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 160.0, 133.6, 114.2, 113.9, 83.7, 75.8, 55.3; IR (film): ν (cm^{-1}) 3290, 2960, 2106, 1607, 1571, 1507, 1171, 1031, 832; MS: *m/z* 132 (M^+, 26), 123 (68), 111 (51), 109 (70), 97 (84), 95 (94), 69 (100), 57 (88), 55 (96).

4-Nitrophenylacetylene[53] **(2e):** Yellow solid, m.p. 146–147 °C (lit.[53] m.p. 147–148 °C). ^{1}H NMR ($CDCl_3$): δ 8.20 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 3.36 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 146.2, 133.0, 128.9, 123.6, 82.3, 81.6; IR (film): ν (cm^{-1}) 3253, 2107, 1594, 1513, 1492, 1344, 855, 752; MS: *m/z* 147 (M^+, 100), 117 (86), 101 (97), 89 (78), 75 (95).

4-Methylphenylacetylene[51] **(2f):** Colourless oil. ^{1}H NMR ($CDCl_3$): δ 7.38 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 3.03 (s, 1H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 139.0, 132.0, 129.1, 119.0, 104.2, 83.8, 21.5; IR (film): ν (cm^{-1}) 3290, 2923, 1631, 1598, 1574, 670; MS: *m/z* 116 (M^+, 23), 101 (45), 97 (51), 91 (64), 71 (68), 69 (80), 57 (100).

4-Hydroxyphenylacetylene **(2g):** Colourless oil. ^{1}H NMR ($CDCl_3$): δ 7.41 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.4 Hz, 2H), 4.93 (br, 1H), 3.02 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 156.3, 133.8, 115.5, 114.2, 104.3, 83.7; IR (film): ν (cm^{-1}) 3289, 2154, 1609, 1585, 1510, 1261, 1093, 836; MS: *m/z* 118 (M^+, 100), 93 (89), 77 (56); Found: C, 81.56; H, 5.35%. Calc. for C_8H_6O: C, 81.34; H, 5.12.

4-Acetylphenylacetylene **(2h):** Colourless oil. ^{1}H NMR ($CDCl_3$): δ 7.91 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 3.25 (s, 1H), 2.61 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 197.3, 136.8, 132.3, 128.2, 126.9, 82.8, 80.3, 26.6; IR (film): ν (cm^{-1}) 3282, 2926, 2162, 1686, 1595, 1494, 761; MS: *m/z* 144 (M^+, 86), 129 (100), 101 (91), 85 (64), 71 (75), 57 (85); Found: C, 83.05; H, 5.33%. Calc. for $C_{10}H_8O$: C, 83.31; H, 5.59.

4-Methoxycarbonylphenylacetylene **(2i):** Colourless oil. ^{1}H NMR ($CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 3.92 (s, 3H), 3.23 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 166.4, 132.1, 130.2, 129.5, 126.8, 82.8, 80.0, 52.3; IR (film): ν (cm^{-1}) 3290, 2925, 2196, 1725, 1608, 1278, 1109, 696; MS: *m/z* 160 (M^+, 57), 146 (32), 129 (100), 101 (71), 75 (34); Found: C, 74.75; H, 4.82%. Calc. for $C_{10}H_8O_2$: C, 74.99; H, 5.03.

3-Nitrophenylacetylene[54] **(2j):** Yellow oil. ^{1}H NMR ($CDCl_3$): δ 8.34 (s, 1H), 8.22–8.19 (m, 1H), 7.81–7.78 (m, 1H), 7.52 (t, J = 8.0 Hz, 1H), 3.22 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 148.1, 137.8, 129.4, 127.0, 124.0, 123.6, 81.1, 79.9; IR (film): ν (cm^{-1}) 3289, 2119, 1574, 1530, 1473, 1352, 807, 736; MS: *m/z* 147 (M^+, 89), 123 (34), 111 (42), 101 (100), 77 (45), 75 (65), 57 (48).

3-Methylphenylacetylene[55] **(2k):** Colourless oil. ^{1}H NMR ($CDCl_3$): δ 7.32–7.16 (m, 4H), 3.04 (s, 1H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 138.0, 132.7, 129.7, 129.2, 128.2, 121.9, 104.2, 83.8, 21.2; IR (film): ν (cm^{-1}) 3291, 2922, 2381, 1631, 1463, 758; MS: *m/z* 116 (M^+, 19), 101 (54), 97 (61), 85 (67), 71 (84), 57 (100).

3-Cyanophenylacetylene **(2l):** Colourless oil. ^{1}H NMR ($CDCl_3$): δ 7.78–7.61 (m, 3H), 7.45 (t, J = 8.0 Hz, 1H), 3.19 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 136.2, 135.5, 132.1, 129.3, 123.8, 117.9, 113.0, 81.2, 79.8; IR (film): ν (cm^{-1}) 3293, 2233, 1641, 1594, 1573, 800; MS: *m/z* 127 (M^+, 100), 101 (84), 75 (41); Found: C, 84.78; H, 3.81%. Calc. for C_9H_5N: C, 85.02; H, 3.96.

1-Ethynylnaphthalene[56] **(2m):** Colourless oil. ^{1}H NMR ($CDCl_3$): δ 8.37–8.35 (m, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.75–7.72 (m, 1H), 7.59–7.40 (m, 3H), 3.47 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 133.5, 133.1, 131.2, 129.3, 128.3, 127.0, 126.5, 126.1, 125.1, 119.8, 81.9, 81.8; IR

(film): ν (cm^{-1}) 3292, 3058, 2102, 1586, 1508, 800, 773; MS: *m/z* 152 (M^+, 23), 127 (68), 83 (59), 69 (64), 57 (100).

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