Three-component coupling of benzyne: Domino intermolecular carbopalladation

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Supporting Information

Part A: Experimental Procedures

General
NMR spectra were recorded on a Brüker dpx360 (360 MHz) instrument and calibrated to residual solvent peaks: proton (CDCl₃ 7.26 ppm or DMSO 2.50 ppm) and carbon (CDCl₃ 77.0 ppm or DMSO 39.4 ppm). The ¹H data is presented as follows: chemical shift (in ppm on the δ scale), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), the coupling constant (J, in Hertz) and integration. The ¹³C data is reported as the ppm on the δ scale followed by the interpretation. IR spectra were recorded on a JASCO FT/IR-460 plus instrument using 4 mm sodium chloride disks. The wavelengths of the maximum absorbance (ν max) are quoted in cm⁻¹. Electrospray high resolution mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea, using a Finnigan MAT 900 XLT double focusing mass spectrometer and at Organon Laboratories using an Applied Biosystems Mariner time of flight mass spectrometer. The data is recorded as the ionisation method followed by the calculated and measured masses. TLC was performed on Merck 60F254 silica plates and visualised by UV light and/or anisaldehyde or potassium permanganate stains. The compounds were purified by wet flash chromatography using Merck Kieselgel 60 (particle size 35-70) silica under a positive pressure. The eluent is quoted as a percentage. All solvents were dried before use unless otherwise stated. DME was distilled over sodium with benzophenone as an indicator. DCM was distilled over calcium hydride. 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulphonate was prepared according to published procedure.¹ All other chemicals were purchased from a chemical supplier and used as received.

1. TCC of allyl chloride, benzyne and methyl acrylate

![Chemical structure]

Catalyst Screen

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All reactions carried out in acetonitrile.

Solvent Screen

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<td>34</td>
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<td>1,4-dioxane</td>
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<td>Starting material</td>
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<tr>
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<td>DME/1,4-dioxane</td>
<td>1:1</td>
<td>Starting material</td>
</tr>
<tr>
<td>8</td>
<td>THF</td>
<td></td>
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<tr>
<td>9</td>
<td>DMF</td>
<td></td>
<td>0&lt;sup&gt;c&lt;/sup&gt;</td>
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Catalyst system: Pd(OAc)2/dppe 5 mol%. MeCN added slowly over 6 hours. Neither product or starting material evident in crude NMR.

TCC of benzyne, allyl chloride and methyl acrylate

Methyl acrylate (0.49 mmol, 2.4 equiv) and allyl chloride (0.25 mmol, 1.2 equiv) were added to a stirred suspension of Pd(OAc)2 (4 mg, 5 mol %), dppe (4 mg, 5 mol %) and CsF (4 equiv) in freshly distilled DME (1.5 mL) under N2 in a 5 mL round bottomed flask. This was followed by the dropwise addition of 2-(trimethylsilyl)phenyl trifluoromethane sulfonate (1) (0.21 mmol, 1 equiv). The reaction was heated to 50 °C and stirred overnight. The reaction mixture was diluted with DCM and filtered through a short plug of silica then concentrated under reduced pressure. Purification by flash column chromatography on silica gel, eluting with 10% EtOAc/hexanes yielded the title compound.

(E)-methyl 3-(2-allylphenyl)acrylate (7): Isolated as a colourless oil in a yield of 50%. 1H NMR (CDCl3, 360 MHz) δ 8.06 (d, 1H, J = 15.8), 7.58 (dd, 1H, J = 7.5, 1.4), 7.33 (dd, 1H, J = 7.2, 1.4), 7.32 – 7.25 (m, 2H), 6.37 (d, 1H, J = 15.8), 5.96 (m, 1H), 5.08 (dd, 1H, J = 10.1, 1.6), 5.00 (dd, 1H, J = 15.3, 1.7), 3.83 (s, 3H), 3.58 (d,
$^{2}$H, $J = 7.7$; $^{13}$C NMR (CDCl$_3$, 62.9 MHz) $\delta$ 167.4 (quat), 142.4 (CH), 139.2 (quat), 136.5 (CH), 133.3 (quat), 130.3 (CH), 130.2 (CH), 126.8 (CH), 126.6 (CH), 119.1 (CH), 116.4 (CH$_2$), 51.7 (CH$_3$), 37.4 (CH$_2$); IR (film/cm$^{-1}$) 2949, 1717, 1634, 1434, 1318, 1272, 1194, 1171; HRMS (ES$^+$) calcd. for C$_{13}$H$_{15}$O$_2$: (M+H)$^+$ 203.1067; found 203.1067.

2. TCC of methyl bromoacetate, benzyne and acrylates

$$\text{R}_1\text{Br} + \text{R}_2\text{OC} = \text{Ru} + \text{CsF (4.5 equiv)}$$

\[ \text{R}_1\text{Me} \]

Catalyst Screen

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<th>Entry</th>
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<th>Ligand</th>
<th>Yield of 12 (%)</th>
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<td>dppf</td>
<td>Complex mix</td>
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<td>7</td>
<td>Pd$_2$(dba)$_3$</td>
<td>dppp</td>
<td>65</td>
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<td>8</td>
<td>Pd$_2$(dba)$_3$</td>
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<td>57</td>
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<td>Pd(dppe)$_2$</td>
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TCC of 1, 10 and methyl acrylate was carried out in MeCN with Pd(dppf)Cl$_2$ as catalyst. None of the desired product, 12a, could be isolated.

**General method for TCC of benzyne, bromoacetates and acrylates**

Methyl acrylate (0.31 mmol, 1.5 equiv) and methyl bromoacetate, 10, (0.21 mmol, 1 equiv) were added to a stirred suspension of Pd(dppf)Cl$_2$ (8.4 mg, 5 mol%) and CsF (4.5 equiv) in freshly distilled DME (1 ml) under N$_2$. This was followed by the dropwise addition of 2-(trimethylsilyl)phenyl trifluoromethane sulfonate (1) (0.31 mmol, 1.5 equiv). The reaction was stirred at 50 ºC over two nights, after which time it was diluted with DCM and filtered through a short plug of silica then concentrated under reduced pressure. Flash chromatography on silicagel, eluting with 20% EtOAc/hexanes yielded the title compounds.

(E)-methyl 3-(2-((methoxycarbonyl)methyl)phenyl)acrylate (12a): Isolated as a colourless oil in a yield of 75%. $^1$H NMR (CDCl$_3$, 360 MHz) $\delta$ 7.96 (d, 1H, $J = 15.8$), 7.60 (dd, 1H, $J = 1.6, 7.3$), 7.38 - 7.27 (m, 3H), 6.38 (d, 1H, $J = 15.8$), 3.81 (s, 3H), 3.81 (s, 2H), 3.70 (s, 3H); $^{13}$C NMR (CDCl$_3$, 90.55 MHz) $\delta$ 171.3 (quat), 167.1 (quat), 141.8 (CH), 133.9 (quat), 133.5 (quat), 131.1 (CH), 130.1 (CH), 127.9 (CH), 126.9 (CH), 120.0 (CH), 52.2 (CH$_3$), 51.7 (CH$_3$), 38.6 (CH$_2$); IR (film/cm$^{-1}$) 2952, 1716, 1634, 1434, 1319, 1170; HRMS (ES$^+$) calcd. for C$_{13}$H$_{15}$O$_4$: (M+H)$^+$ 235.0965. Found: 235.0967.

(E)-tert-butyl 3-(2-((methoxycarbonyl)methyl)phenyl)acrylate (12b): Isolated as a colourless oil in a yield of 80%. $^1$H NMR (CDCl$_3$, 360 MHz) $\delta$ 7.86 (d, 1H, $J = 15.7$), 7.59 (m, 1H), 7.37 - 7.25 (m, 3H), 6.31 (d, 2H, $J = 15.8$), 3.81 (s, 3H), 3.81 (s, 2H), 3.70 (s, 3H); $^{13}$C NMR (CDCl$_3$, 90.55 MHz) $\delta$ 171.3 (quat), 167.1 (quat), 141.8 (CH), 133.9 (quat), 133.5 (quat), 131.1 (CH), 130.1 (CH), 127.9 (CH), 126.9 (CH), 120.0 (CH), 52.2 (CH$_3$), 51.7 (CH$_3$), 38.6 (CH$_2$); IR (film/cm$^{-1}$) 2952, 1716, 1634, 1434, 1319, 1170; HRMS (ES$^+$) calcd. for C$_{13}$H$_{15}$O$_4$: (M+H)$^+$ 235.0965. Found: 235.0967.
15.7), 3.78 (s, 2H), 3.70 (s, 3H), 1.52 (s, 9H); $^{13}$C NMR (CDCl$_3$, 90.55 MHz) δ 171.3 (quat), 165.9 (quat), 140.3 (CH), 134.0 (quat), 133.2 (quat), 130.8 (CH), 127.6 (CH), 126.7 (CH), 122.2 (CH), 80.4 (quat), 52.0 (CH$_3$), 38.4 (CH$_2$), 28.0 (CH$_3$); IR (film/cm$^{-1}$) 2978, 1740, 1708, 1633, 1321, 1151; HRMS (ES$^+$) cald. for C$_{16}$H$_{21}$O$_4$: (M+H)$^+$ 277.1434. Found: 277.1435.

(E)-$^{3}$-tert-butyl 3-((methoxycarbonyl)methyl)-4-methylphenyl)acrylate (12c) and (E)-$^{3}$-tert-butyl 3-((methoxycarbonyl)methyl)-5-methylphenyl)acrylate (12d): Isolated as a colourless oil in a yield of 70%. $^{1}$H NMR (CDCl$_3$, 360 MHz) δ 7.75 (d, 1H, J = 15.7), 7.42 (d, 0.5H, J = 7.9), 7.34 (s, 0.5H), 7.07 (m, 3H), 6.22 (d, 0.5H, J = 15.7), 6.20 (d, 0.5H, J = 15.7), 3.66 (s, 1H), 3.64 (s, 1H), 3.63 (s, 1.5H), 3.61 (s, 1.5H), 2.27 (s, 3H), 1.44 (s, 9H); $^{13}$C NMR (CDCl$_3$, 90.55 MHz) δ 171.6 (quat), 171.6 (quat), 166.2 (quat), 166.1 (quat), 140.6 (CH), 140.3 (CH), 140.2 (quat), 137.4 (quat), 133.8 (quat), 133.3 (quat), 131.7 (CH), 131.2 (quat), 130.9 (CH), 130.7 (CH), 130.5 (quat), 128.6 (CH), 127.4 (CH), 126.7 (CH), 122.0 (CH), 121.2 (CH), 80.5 (quat), 80.4 (quat), 52.2 (CH$_3$), 52.1 (CH$_3$), 38.5 (CH$_2$), 38.1 (CH$_2$), 28.1 (CH$_3$), 21.2 (CH$_3$), 21.0 (CH$_3$); IR (film/cm$^{-1}$) 2978, 1741, 1707, 1633, 1321, 1251, 1151; HRMS (ES$^+$) cald for C$_{13}$H$_{13}$O$_3$: (M-OtBu)$^+$ 217.0859. Found: 217.0852.

3. TCC of benzyl bromides, benzyne and *tert*-butyl acrylate

![Catalyst Screen](attachment:image.png)

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<td>1:1 15 with phenanthrene</td>
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<td>Pd(OAc)$_2$</td>
<td>dppe</td>
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<td>64% yield of 15</td>
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<td>47% yield of 15</td>
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TCC of 13b, 1 and 14 was also carried out in MeCN using the Pd(OAc)$_2$/dppe catalyst system. Product 15b was isolated in a yield of 27%.

**General method for TCC of benzyl bromides, benzyne and acrylates**

Benzyl bromide (0.31 mmol, 1.5 equiv) and *tert*-butyl acrylate (0.21 mmol, 1 equiv) were added to a stirred suspension of Pd(OAc)$_2$ (2.4 mg, 5 mol %), dppe (4.3 mg, 5 mol %) and CsF (3 equiv) in freshly distilled DME (1 mL) under N$_2$. This was followed by the dropwise addition of 2-(trimethylsilyl)phenyl trifluoromethane sulfonate (1) (0.21 mmol, 1 equiv). The reaction was stirred at 50 ºC over 2 nights. The reaction mixture was diluted with DCM and filtered through a pad of silica. Purification was achieved either by a) chromatography on silica gel eluting with EtOAc/hexanes to produce the ester, or b) treatment with TFA (0.3 mL) in DCM (1 mL) at room temperature followed by concentration under reduced pressure to afford a residue which could be triturated and / or recrystallised from hexane/EtOAc mixtures to afford the crystalline acids.

(E)-3-(2-benzylphenyl)acrylic acid (15a): Isolated in 65% yield as a colourless solid: m.p. (hexanes) 126 - 128 ºC; $^{1}$H NMR (DMSO, 360 MHz) δ 7.89 (d, 1H, J = 15.8), 7.77 (d, 1H, J = 7.6), 7.43 - 7.34 (m, 5H), 7.19 (m,
$^1$H NMR (CDCl$_3$, 360 MHz) δ 7.98 (d, 1H, J = 15.8), 7.62 (dd, 1H, J = 7.4, 1.1), 7.42 - 7.34 (m, 2H), 7.32 (d, 2H, J = 8.3), 7.43 - 7.31 (m, 3H), 7.08 (d, 2H, J = 8.3), 6.41 (d, 1H, J = 15.8), 4.14 (s, 2H); $^{13}$C NMR (CDCl$_3$, 90.55 MHz) δ 165.9 (quat), 157.7 (quat), 140.9 (quat), 140.2 (CH), 133.4 (quat), 130.6 (CH), 129.2 (CH), 127.4 (CH), 126.8 (CH), 122.1 (CH), 80.5 (quat), 38.7 (CH$_2$), 27.9 (CH$_3$); IR (film/cm$^{-1}$) 2977, 1707, 1519, 1346, 1151; HRMS (ES +) cald for C$_{21}$H$_{25}$O$_3$: (M+H)$^+$ 325.1798. Found: 325.1802.

(E)-3-(2-(4-bromobenzyl)phenyl)acrylic acid (15d): Isolated in a yield of 80% as a light yellow solid; m.p. (hexanes) 174 ºC; $^1$H NMR (DMSO, 360 MHz) δ 7.99 (d, 1H, J = 15.8), 7.69 (d, 1H, J = 6.4, 1.4), 7.48 (d, 2H, J = 8.3), 7.43 - 7.31 (m, 3H), 7.08 (d, 2H, J = 8.3), 6.41 (d, 1H, J = 15.8), 4.14 (s, 2H); $^{13}$C NMR (DMSO, 90.55 MHz) δ 167.3 (quat), 141.0 (CH), 139.9 (quat), 139.4 (quat), 132.9 (quat), 131.3 (CH), 130.9 (CH), 130.6 (CH), 130.2 (CH), 127.2 (CH), 126.9 (CH), 120.5 (CH), 115.3 (CH), 37.4 (CH$_2$); IR (film/cm$^{-1}$) 2977, 1707, 1519, 1346, 1151; HRMS (ES -) cald for C$_{16}$H$_{12}$O$_2$Br: (M-H)$^-$ 315.0015. Found: 315.0022.

(E)-3-(2-(4-fluorobenzyl)phenyl)acrylic acid (15e): Isolated as a colourless solid in a yield of 69%. m.p (hexanes) 147 ºC; $^1$H NMR (DMSO, 360 MHz) δ 7.86 (d, 1H, J = 15.8), 7.76 (d, 1H, J = 7.9), 7.41 (t, 2H, J = 7.3), 7.18 - 7.09 (m, 4H), 6.41 (d, 1H, J = 15.8), 4.16 (s, 2H); $^{13}$C NMR (DMSO, 90.55 MHz) δ 167.3 (quat), 141.0(CH), 139.8(quat), 136.6 (quat), 130.8 (CH), 130.1 (CH), 130.0 (CH), 127.1 (CH), 126.5 (CH), 120.5 (CH), 115.3 (CH), 37.2 (CH$_2$); IR (film/cm$^{-1}$) 2977, 1707, 1416, 1418, 1281, 1217; HRMS (ES') cald for C$_{16}$H$_{12}$O$_2$F: (M-OtBu)$^+$ 266.0812. Found: 266.0815.

(E)-3-(2-(3-chlorobenzyl)phenyl)acrylic acid (15f): Isolated as a white powdery solid in a yield of 91%. m.p. (hexanes) 142 ºC; $^1$H NMR (DMSO, 360 MHz) δ 7.86 (d, 1H, J = 15.8), 7.77 (dd, 1H, J = 8.7, 1.7), 7.43 (m, 1H), 7.36 - 7.30 (m, 3H), 7.26 (m, 1H), 7.18 (t, 1H, J = 1.7), 7.09 (bd, 1H, J = 7.6), 6.41 (d, 1H, J = 15.8), 4.18 (s, 2H); $^{13}$C NMR (DMSO, 90.55 MHz) δ 167.2 (quat), 143.0 (quat), 140.9 (CH), 139.1 (quat), 133.0 (quat), 132.9 (quat), 130.8 (CH), 130.2 (CH), 128.1 (CH), 127.2 (CH), 127.0 (CH), 126.9 (CH), 126.0 (CH), 120.6 (CH), 37.5 (CH$_2$); IR (film/cm$^{-1}$) 2977, 1707, 1416, 1279, 1223; HRMS (ES') cald for C$_{16}$H$_{12}$O$_2$Cl: (M-H)$^-$ 271.0520. Found: 271.0520.

(E)-3-(2-(4-cyanobenzyl)phenyl)acrylic acid (15g): Isolated as a colourless powder solid in a yield of 89%. m.p. (hexanes) 142 ºC; $^1$H NMR (DMSO, 360 MHz) δ 7.86 (d, 1H, J = 15.8), 7.77 (dd, 1H, J = 8.7, 1.7), 7.43 (m, 1H), 7.36 - 7.30 (m, 3H), 7.26 (m, 1H), 7.18 (t, 1H, J = 1.7), 7.09 (bd, 1H, J = 7.6), 6.41 (d, 1H, J = 15.8), 4.18 (s, 2H); $^{13}$C NMR (DMSO, 90.55 MHz) δ 167.2 (quat), 143.0 (quat), 140.9 (CH), 139.1 (quat), 133.0 (quat), 132.9 (quat), 130.8 (CH), 130.2 (CH), 128.1 (CH), 127.2 (CH), 127.0 (CH), 126.9 (CH), 126.0 (CH), 120.6 (CH), 37.5 (CH$_2$); IR (film/cm$^{-1}$) 2977, 1707, 1416, 1279, 1223; HRMS (ES') cald for C$_{16}$H$_{12}$O$_2$Cl: (M-H)$^-$ 271.0520. Found: 271.0520.
(E)-3-(2-(4-(trifluoromethyl)benzyl)phenyl)acrylic acid (15i): Isolated as a colourless crystalline solid in a yield of 67%; m.p (water) 122 – 123 ºC; ^1H NMR (DMSO, 360 MHz) δ 7.85 (d, 1H, J = 15.8), 7.76 (d, 1H, J = 7.7), 7.40 (q, 1H, J = 8.3), 7.33 - 7.30 (m, 2H), 7.20 (t, 1H, J = 7.7), 7.78-6.67 (m, 3H), 6.41 (d, 1H, J = 15.8), 4.11 (s, 2H), 3.71 (s, 3H); 13C NMR (DMSO, 90.55 MHz) δ 167.4 (quat), 141.3 (CH), 139.8 (quat), 138.2 (quat), 133.1 (quat), 133.0 (quat), 131.6 (quat), 131.0 (CH), 130.3 (CH), 129.5 (CH), 127.4 (CH), 127.2 (CH), 126.9 (CH), 126.4 (CH), 126.2 (CH), 125.6 (CH), 120.4 (CH), 38.3 (CH2); IR (film/cm⁻¹) 2977, 1707, 1511, 1248, 1150; HRMS (ES⁺) cald for C₁₇H₁₅O₂F₃: (M-OtBu)+ 287.1077. Found: 287.1070.

(E)-3-(2-(3-methoxybenzyl)phenyl)acrylic acid (15j): Isolated as a colourless crystalline solid in a yield of 62%; m.p. (water) 134 – 135 ºC; ^1H NMR (DMSO, 360 MHz) δ 7.91 (d, 1H, J = 15.8), 7.76 (d, 1H, J = 7.7), 7.50 (s, 1H), 7.48 - 7.32 (m, 6H), 6.41 (d, 1H, J = 15.8), 4.11 (s, 2H), 3.71 (s, 3H); 13C NMR (DMSO, 90.55 MHz) δ 167.4 (quat), 141.3 (CH), 139.8 (quat), 138.2 (quat), 133.1 (quat), 133.0 (quat), 131.6 (quat), 131.0 (CH), 130.3 (CH), 128.0 (CH), 127.5 (CH), 127.4 (CH), 127.2 (CH), 126.9 (CH), 126.4 (CH), 126.2 (CH), 125.6 (CH), 120.4 (CH), 38.3 (CH2); IR (film/cm⁻¹) 2977, 1740, 1707, 1321, 1150; HRMS (ES⁺) cald for C₁₇H₁₅O₃: (M-H)⁻ 267.1016. Found: 267.1016.

(E)-3-(2-(naphthalen-3-yl)methyl)phenyl)acrylic acid (15k): Isolated as a colourless powdery solid in a yield of 92%; m.p. (hexane) 160-161 ºC; ^1H NMR (CDCl₃, 360 MHz) δ 7.92 (d, 1H, J = 15.8), 7.50 (d, 0.5H, J = 7.9), 7.41 (bs, 0.5 H), 7.19 - 7.12 (m, 3.5H), 7.02 (bs, 0.5H), 6.85 - 6.80 (m, 2H), 6.26 (d, 0.5H, J = 15.8), 6.24 (d, 0.5H, J = 15.8), 4.05 (s, 2H), 3.77 (s, 3H), 1.53 (s, 9H); 13C NMR (CDCl₃, 90.55 MHz) δ 166.3 (quat), 166.2 (quat), 157.8 (quat), 157.8 (quat), 141.2 (quat), 141.0 (quat), 140.3 (CH), 140.0 (CH), 137.5 (quat), 136.1 (quat), 133.3 (quat), 132.5 (quat), 132.4 (quat), 131.3 (CH), 130.7 (CH), 130.6 (CH), 130.5 (CH), 129.5 (CH), 127.6 (CH), 127.1 (CH), 126.5 (CH), 121.2 (CH), 120.4 (CH), 113.8 (CH), 80.2 (quat), 80.2 (quat), 55.1 (CH₃), 38.0 (CH₂), 37.7 (CH₃), 28.1 (CH₃), 21.3 (CH₃), 20.9 (CH₃); IR (film/cm⁻¹) 2977, 1707, 1511, 1248, 1150; HRMS (ES⁺) cald for C₁₉H₁₂O₂: (M-OtBu)⁺ 265.1223. Found: 265.1213.
Part B: Spectroscopic Data
15g

\[
\begin{array}{c}
168.771 \\
148.013 \\
142.344 \\
140.202 \\
134.518 \\
133.923 \\
132.533 \\
131.847 \\
130.891 \\
128.953 \\
128.531 \\
122.245 \\
120.359 \\
110.438 \\
39.540 \\
\end{array}
\]