

Supplementary Information:

**Selective arene functionalization through sequential oxidative and
non-oxidative Heck reactions**

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General remarks

^1H NMR spectra were obtained at 300 MHz in CDCl_3 with CHCl_3 ($\delta = 7.26$ ppm) as an internal standard, in $\text{DMSO}-d_6$ with $\text{DMSO}-d_6$ ($\delta = 2.50$ ppm) as an internal standard, or in $\text{MeOD}-d_4$ with methanol- d_4 ($\delta = 2.05$ ppm) as an internal standard. Coupling constants (J) are given in Hz. Signal assignments refer to numbering schemes which are detailed in the supporting information. ^{13}C NMR spectra were recorded at 75 MHz in CDCl_3 with CDCl_3 ($\delta = 77.0$ ppm) as an internal standard, in $\text{DMSO}-d_6$ with $\text{DMSO}-d_6$ ($\delta = 39.5$ ppm) as an internal standard, or in methanol- d_4 with $\text{CD}_3\text{C}(\text{O})\text{CD}_3$ ($\delta = 29.9$ ppm) as an internal standard. IR spectra were recorded as films on NaCl or KBr plates or as KBr-discs. Wavenumbers (ν) are given in cm^{-1} . Mass spectra were obtained at 70 eV.

General procedure for the *Fujiwara-Moritani* reaction:

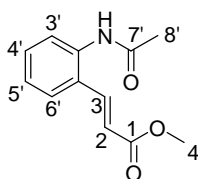
Method A

To a solution of acetamide **1** (1.0 mmol), K₂S₂O₈ (1.0 mmol, 270 mg) and Pd(OAc)₂ (5 mol%, 11.2 mg) in a mixture of methylene chloride (1 mL) and TFA (4 mL) was added methylacrylate (2.0 mmol, 172 mg, 180 µL). The solution was stirred for 20 h at room temperature. The reaction was quenched with 2 mL methylene chloride, neutralized with saturated Na₂CO₃-solution and extracted three times with methylene chloride (each time with 15 mL). The combined organic layers were dried with MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography.

Method B

To a solution of acetamide **1** (1.0 mmol), benzoquinone (1.0 mmol, 108 mg), 4-methylbenzenesulfonic acid (0.5 mmol, 95 mg) and Pd(OAc)₂ (5 mol%, 11.2 mg) in a mixture of toluene (1 mL) and acetic acid (2 mL) was added methyl acrylate (1.2 mmol, 103 mg, 108 µL). The solution was stirred for 20 h at room temperature. The reaction was quenched with 2 mL ethyl acetate, neutralized with 4 N NaOH and extracted three times with ethyl acetate (each time with 15 mL). The combined organic layers were dried with MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography.

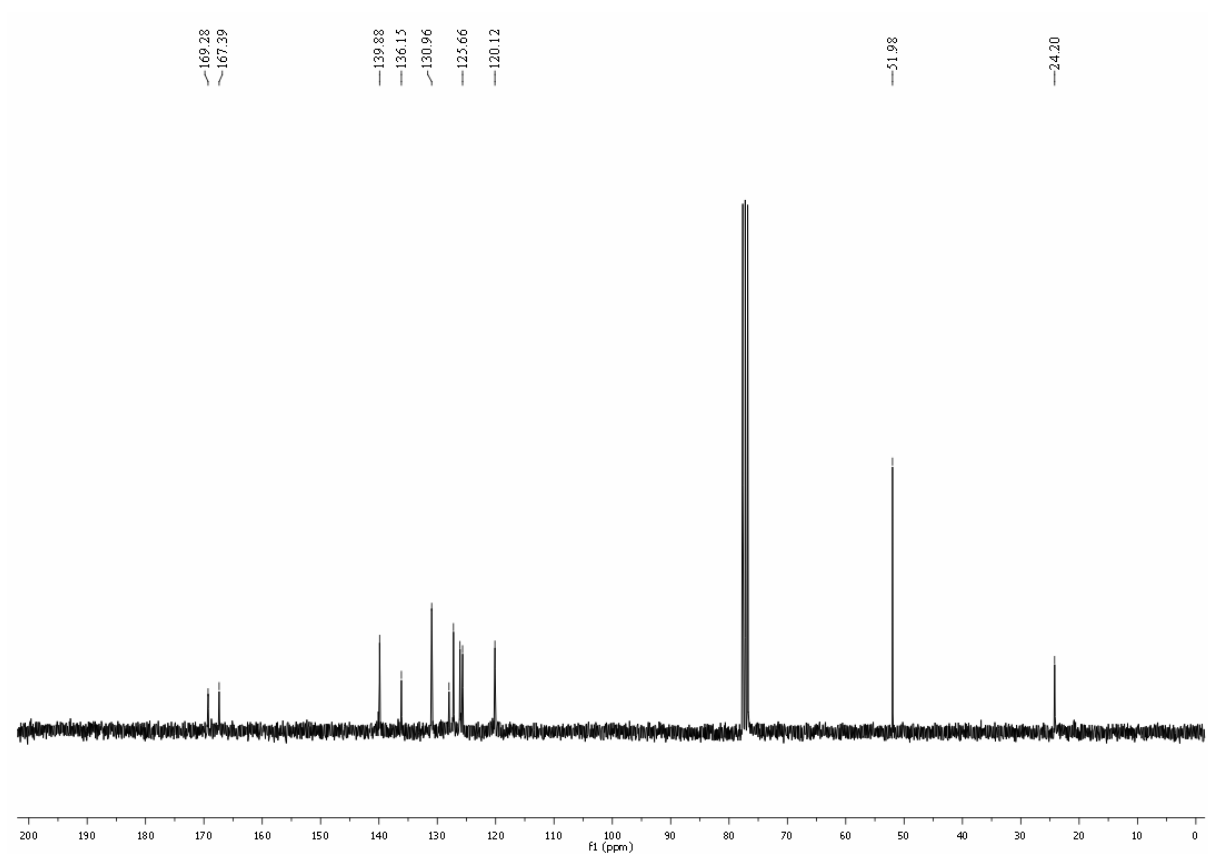
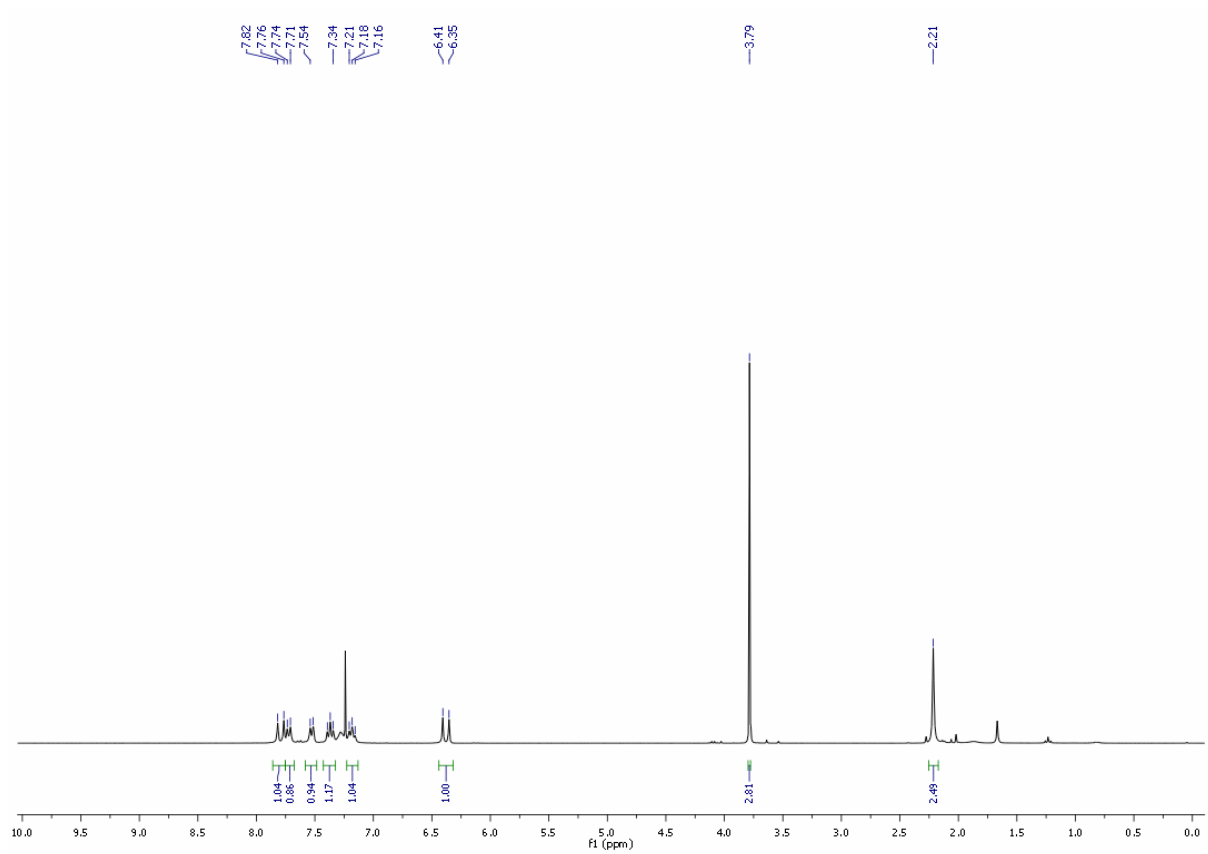
(*E*)-Methyl 3-(2-acetamidophenyl)acrylate (**2a**)



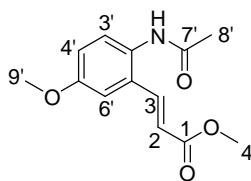
Following the general procedure (method A), (*E*)-methyl 3-(2-acetamidophenyl)acrylate (**2a**) was obtained from acetanilide (**1a**) (1.0 mmol, 135 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane / ethyl acetate 2 : 1) to afford **2a** as a colourless solid (89 %, 0.89 mmol, 196 mg).

¹H NMR (300 MHz, CDCl₃) δ 7.81 (d, J = 15.8 Hz, 1H, 3-H), 7.74 (d, J = 8.0 Hz, 1H, 3'-H), 7.55 (d, J = 7.7 Hz, 1H, 6'-H), 7.39 (t, J = 7.5 Hz, 1H, 4'/5'-H), 7.20 (t, J = 7.5 Hz, 1H, 5'/4'-H), 6.40 (d, J = 15.8 Hz, 1H, 2-H), 3.81 (s, 3H, 4-H), 2.23 (s, 3H, 8'-H). **¹³C NMR (75 MHz, CDCl₃)** δ 169.1, 167.4, 139.9, 136.2, 130.9, 127.9, 127.2, 126.1, 125.7, 120.1, 51.9, 24.2. **MS (EI)** m/z = 219 (3 %), 146 (15 %), 117 (29 %), 43 (100 %). **HRMS (EI)** m/z calcd for C₁₂H₁₃NO₃ [M]⁺: 219.0890, found 219.0902. **Anal.** calcd for C₁₂H₁₃NO₃: C, 65.7 %; H, 6.0 %; N, 6.4 %, found C, 65.2 %; H, 5.8 %; N, 6.3 %. **IR** ν 3254 (m), 2950 (m), 1663 (s), 1193 (s), 1169 (s). **mp** 136°C (Lit.¹: 137-138°C).

¹ V.G. Zaitsev and O.Daugulis *J. Am. Chem. Soc.*, 2005, **127**, 4156.



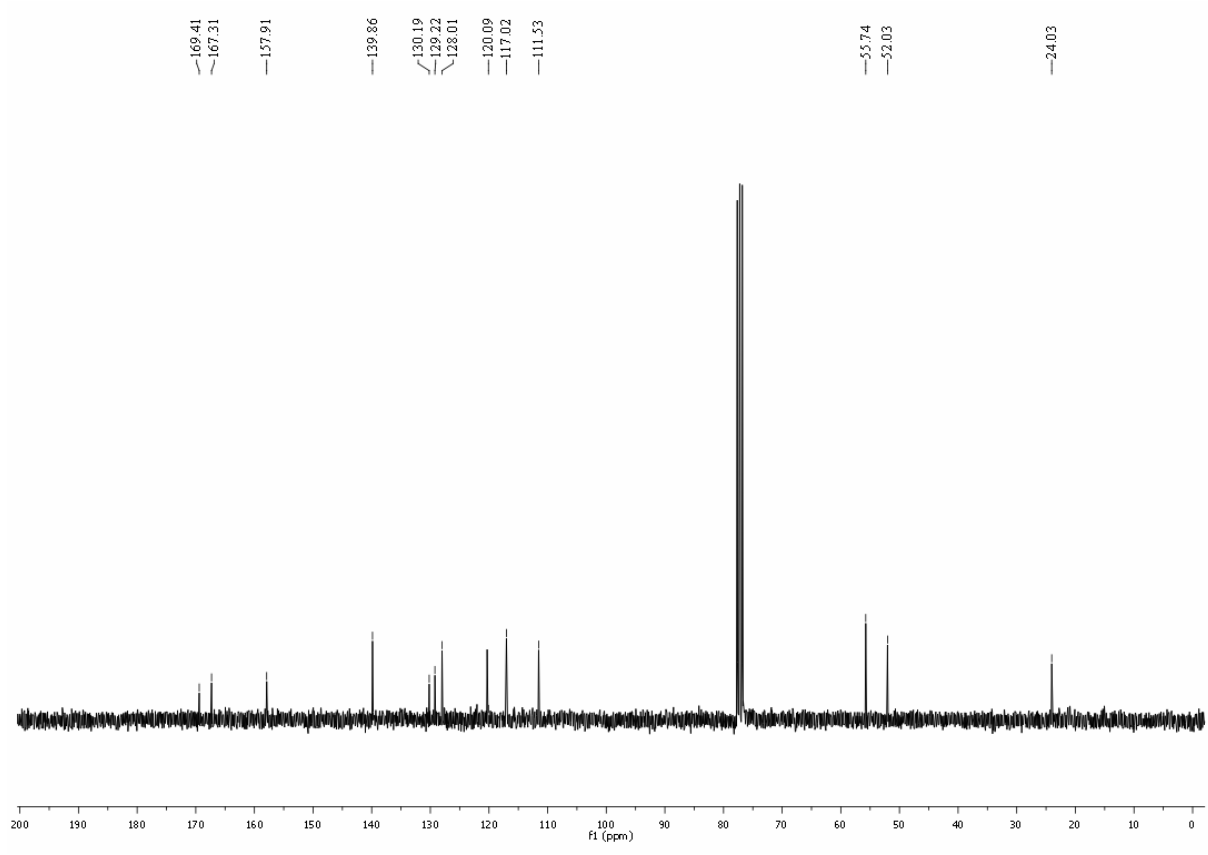
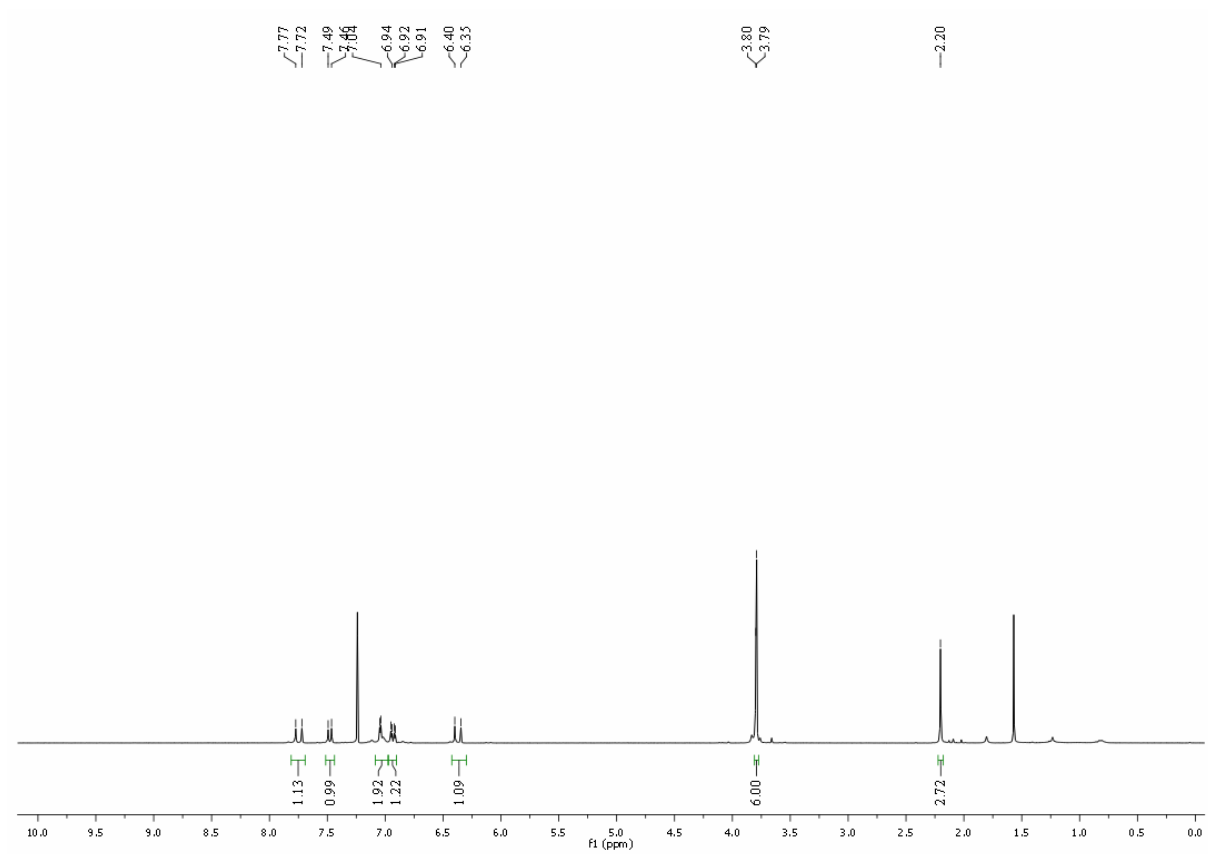
(*E*)-Methyl 3-(2-acetamido-5-methoxyphenyl)acrylate (**2b**)²



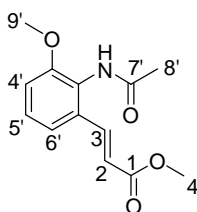
Following the general procedure (method A), (*E*)-methyl 3-(2-acetamido-5-methoxyphenyl)acrylate (**2b**) was obtained from 4-methoxyacetamid (**1b**) (1.0 mmol, 165 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane / ethyl acetate 2 : 1) to afford **2b** as a colourless solid (85 %, 0.85 mmol, 211 mg).

¹H NMR (300 MHz, CDCl₃) δ 7.75 (d, *J* = 15.9 Hz, 1H, 3-H), 7.48 (d, *J* = 8.8 Hz, 1H, 3'-H), 7.04 (d, *J* = 2.8 Hz, 1H, 3'-H), 7.02 (s, 1H, -NH), 6.93 (dd, *J* = 2.9, 8.9 Hz, 1H, 4'-H), 6.38 (d, *J* = 15.8 Hz, 1H, 2-H), 3.80 (s, 3H, 9'H), 3.79 (s, 3H, 4-H), 2.20 (s, 3H, 8'-H). ¹³C NMR (75 MHz, CDCl₃) δ 169.2, 167.1, 157.7, 139.6, 129.9, 129.0, 127.8, 119.9, 116.8, 111.3, 55.5, 51.8, 23.8. MS (EI) *m/z* = 249 (7 %), 176 (25 %), 132 (12 %), 43 (100 %) HRMS (EI) *m/z* calcd for C₁₃H₁₅NO₄ [M]⁺: 249.0996, found 249.0973. Anal. calcd for C₁₃H₁₅NO₄: C, 62.6 %; H, 6.1 %; N, 5.6 %, found C, 61.7 %; H, 6.0 %; N, 5.3 %. IR ν 3252 (m), 2951 (s), 1660 (s), 1286 (s), 1170 (s). mp 168°C.

² B. S. Kim, D. J. Lee, S. W. Youn and C. Jang, *Chem. Asian J.*, 2010, **5**, 2336.

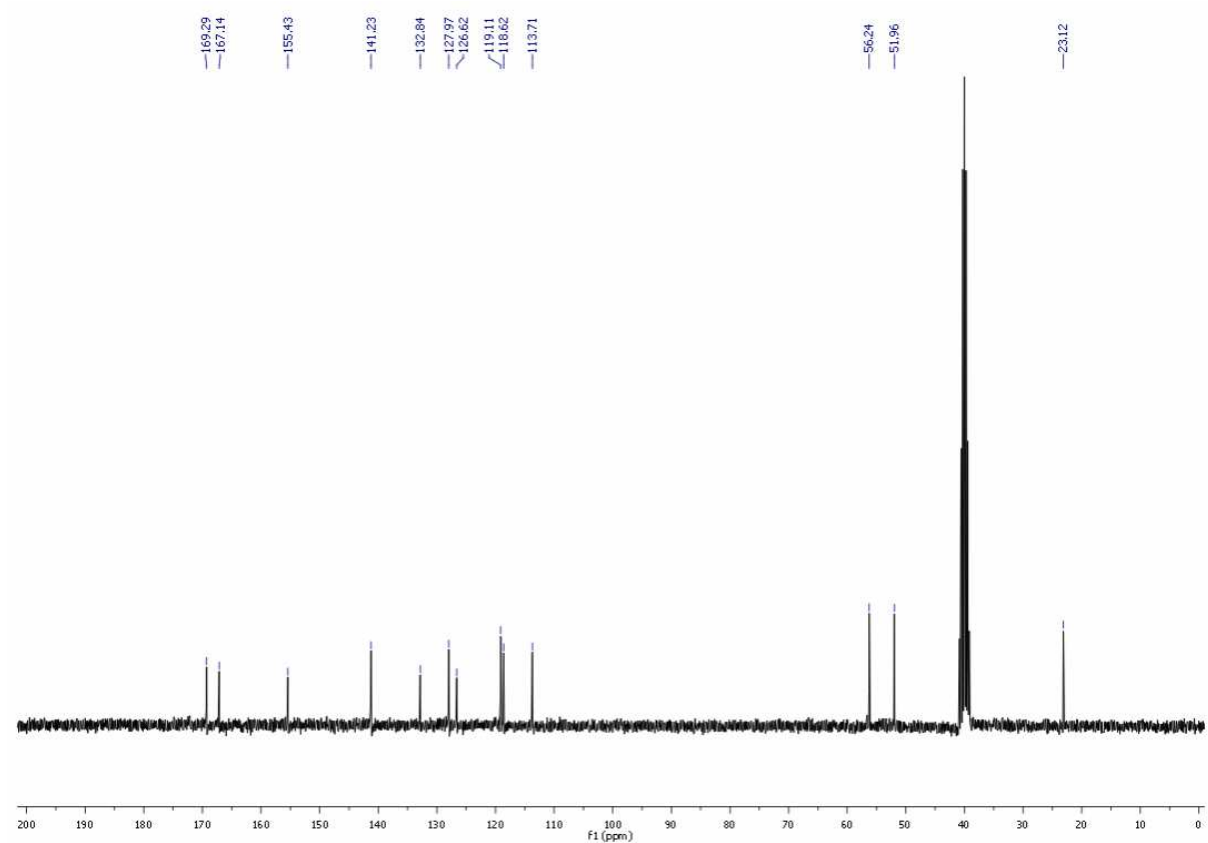
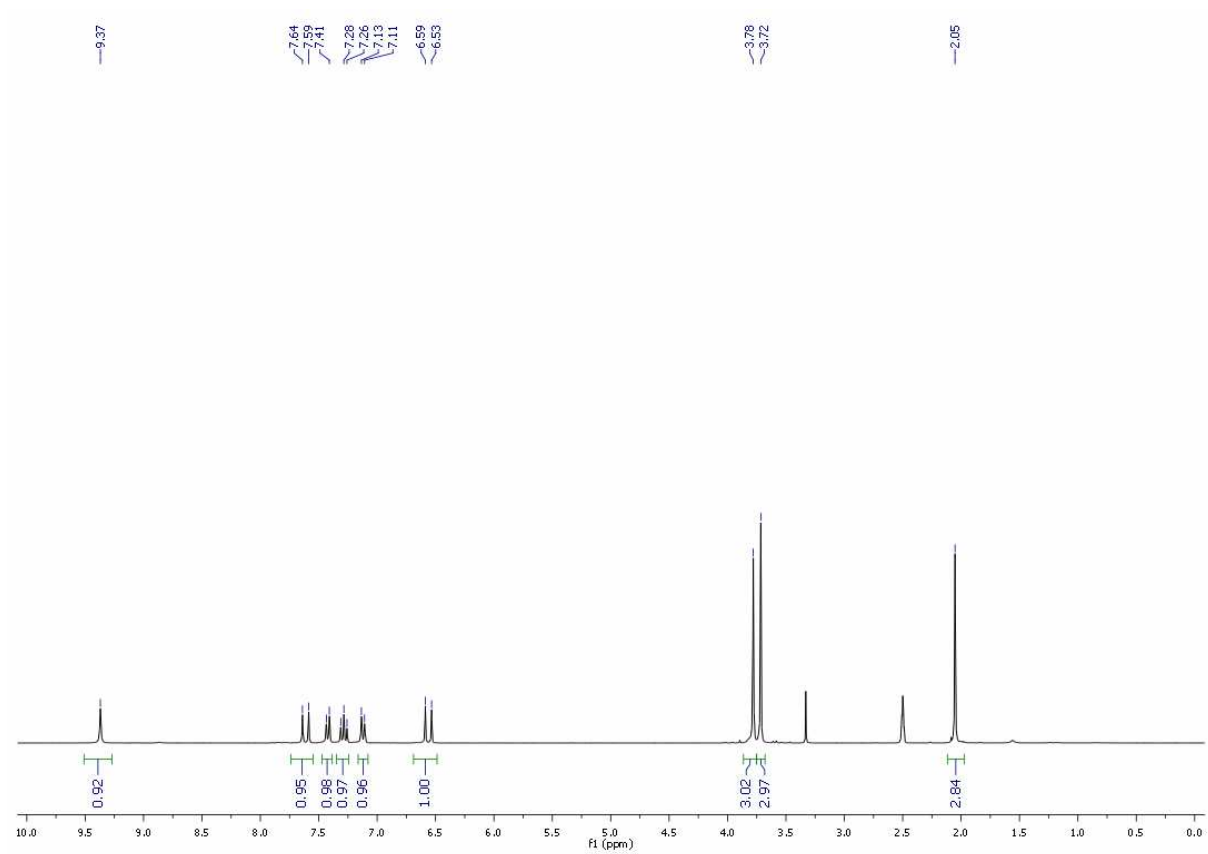


(*E*)-Methyl 3-(2-acetamido-3-methoxyphenyl)acrylate (**2c**)

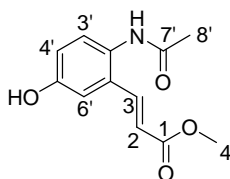


Following the general procedure (method A), (*E*)-methyl 3-(2-acetamido-3-methoxyphenyl)acrylate (**2c**) was obtained from 2-methoxyacetamide (**1c**) (1.0 mmol, 165 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane / ethyl acetate 2 : 1) to afford **2c** as a colourless solid (80 %, 0.80 mmol, 199 mg).

¹H NMR (300 MHz, DMSO) δ 9.37 (s, 1H, -NH), 7.61 (d, *J* = 16.1 Hz, 1H, 3-H), 7.42 (d, *J* = 7.5 Hz, 1H, 6'-H), 7.29 (t, *J* = 8.0 Hz, 1H, 5'-H), 7.12 (d, *J* = 8.1 Hz, 1H, 4'-H), 6.56 (d, *J* = 16.1 Hz, 1H, 2-H), 3.78 (s, 3H, 9'/4-H), 3.72 (s, 3H, 4/9'-H), 2.05 (s, 3H, 8'-H) ¹³C NMR (75 MHz, DMSO) δ 169.3, 167.1, 155.4, 141.2, 132.8, 127.9, 126.6, 119.1, 118.6, 113.7, 56.2, 51.9, 23.1. MS (EI) *m/z* = 249 (23 %), 207 (28 %), 176 (100 %), 43 (26 %) HRMS (EI) *m/z* calcd for C₁₃H₁₅NO₄ [M]⁺: 249.0996, found 249.0973. Anal. calcd for C₁₃H₁₅NO₄: C, 62.6 %; H, 6.1 %; N, 5.6 %, found C, 62.7 %; H, 6.1 %; N, 5.8 %. IR ν 3239 (w), 1712.2 (w), 1267 (m), 1167 (m), 788 (w). mp 158-159°C.

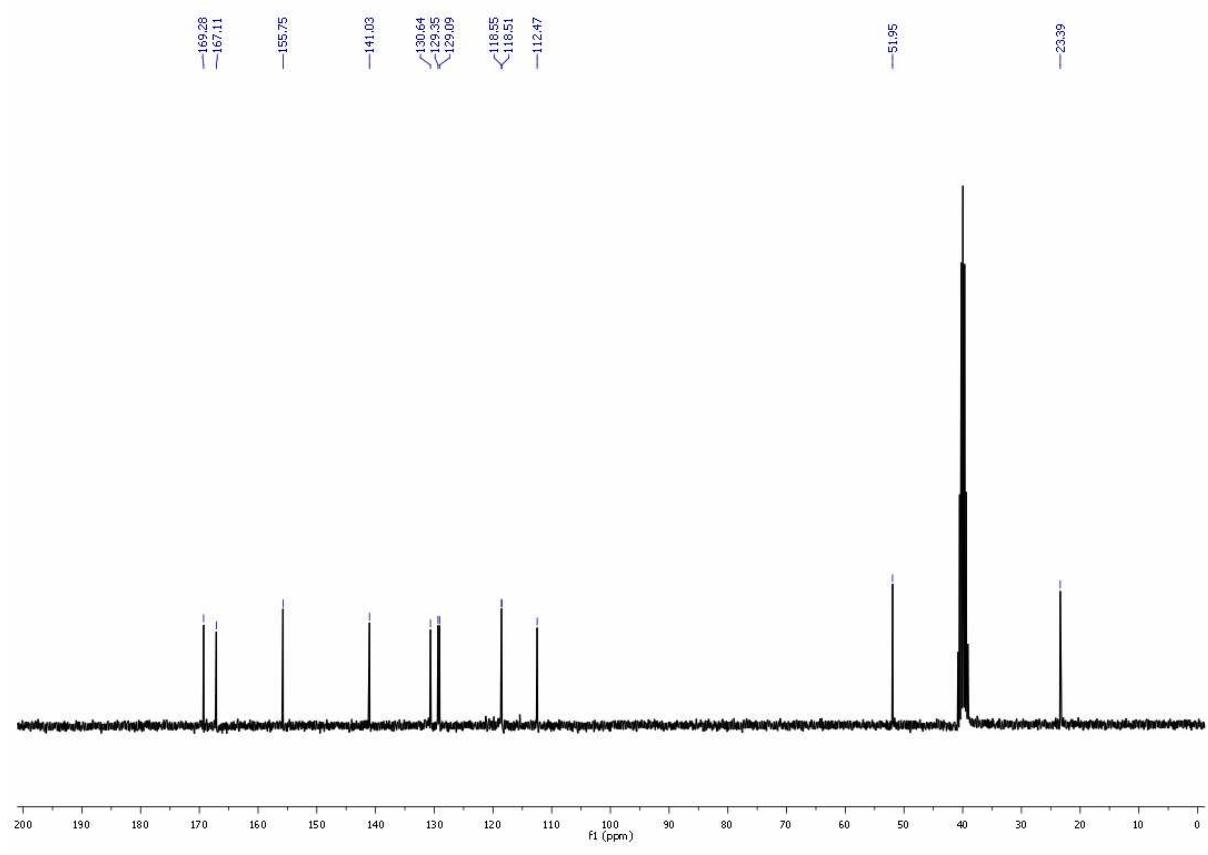
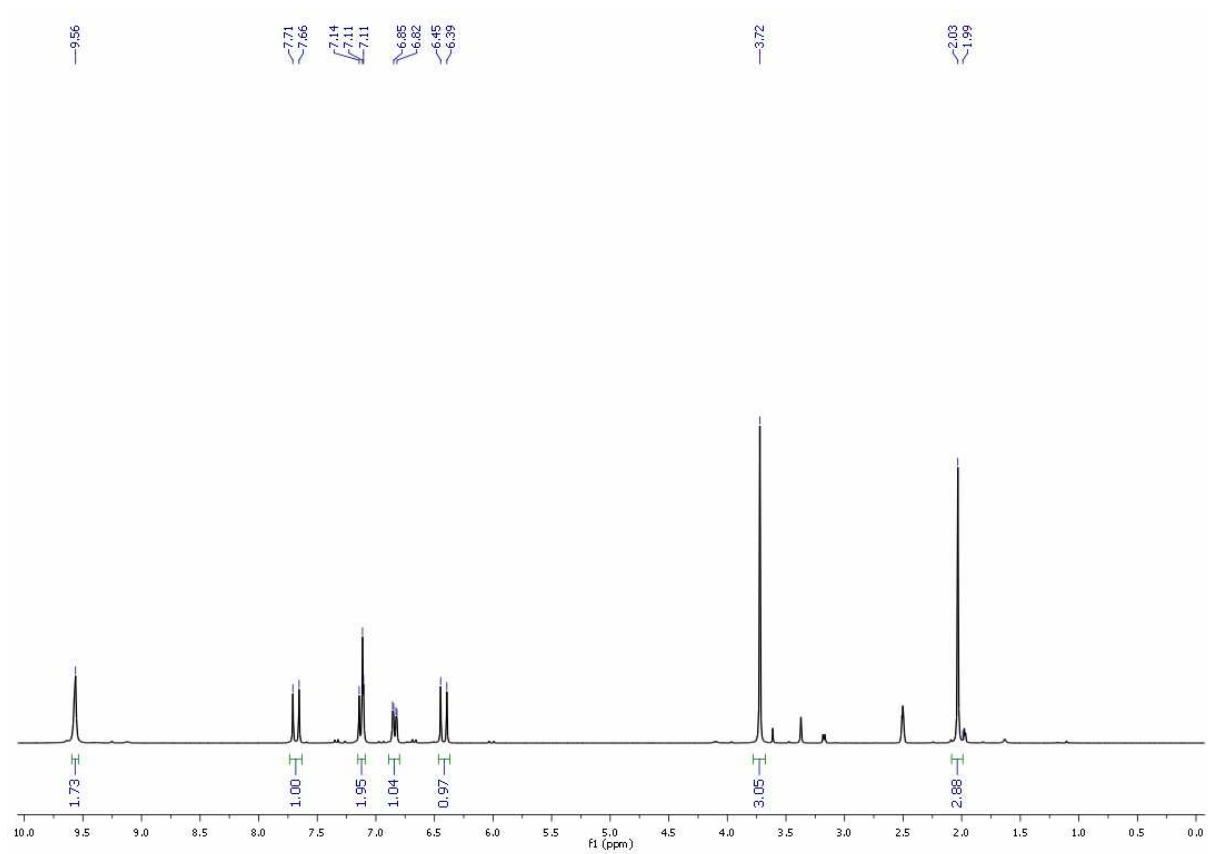


(*E*)-Methyl 3-(2-acetamido-5-hydroxyphenyl)acrylate (**2d**)

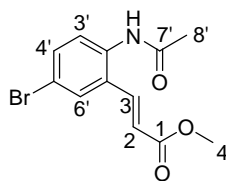


Following the general procedure (method B), (*E*)-methyl 3-(2-acetamido-5-hydroxyphenyl)acrylate (**2d**) was obtained from 4-hydroxyacetamide (**1d**) (10.0 mmol, 1.50 g). The residue was purified by column chromatography (SiO₂, *n*-hexane / ethyl acetate 1 : 1) to afford **2d** as a colourless solid (55 %, 5.5 mmol, 1.30 g).

¹H NMR (300 MHz, DMSO) δ 9.56 (s, -OH), 7.68 (d, *J* = 16.0 Hz, 1H, 3-H), 7.12 (d, *J* = 10.5 Hz, 1H, 3'-H), 7.11 (s, 6'-H), 6.84 (dd, *J* = 2.7, 8.6 Hz, 1H, 4'-H), 6.42 (d, *J* = 16.0 Hz, 1H, 2-H), 3.72 (s, 3H, 4-H), 2.01 (s, 3H, 8'-H). ¹³C NMR (75 MHz, DMSO) δ 169.3, 167.1, 155.8, 141.0, 130.6, 129.4, 129.1, 118.6, 112.5, 51.9, 23.4. MS (EI) *m/z* = 235 (9 %), 162 (35 %), 133 (27 %), 43 (100 %). HRMS (EI) *m/z* calcd for C₁₂H₁₃NO₄ [M]⁺: 235.0839, found 235.0861. Anal. calcd for C₁₂H₁₃NO₄: C, 61.3 %; H, 5.6 %; N, 6.0 %, found C, 60.8 %; H, 5.5 %; N, 5.8 %. IR *y* 3675 (w), 2988 (m), 1066 (s), 1056 (s), 597 (s). mp 197-200°C.

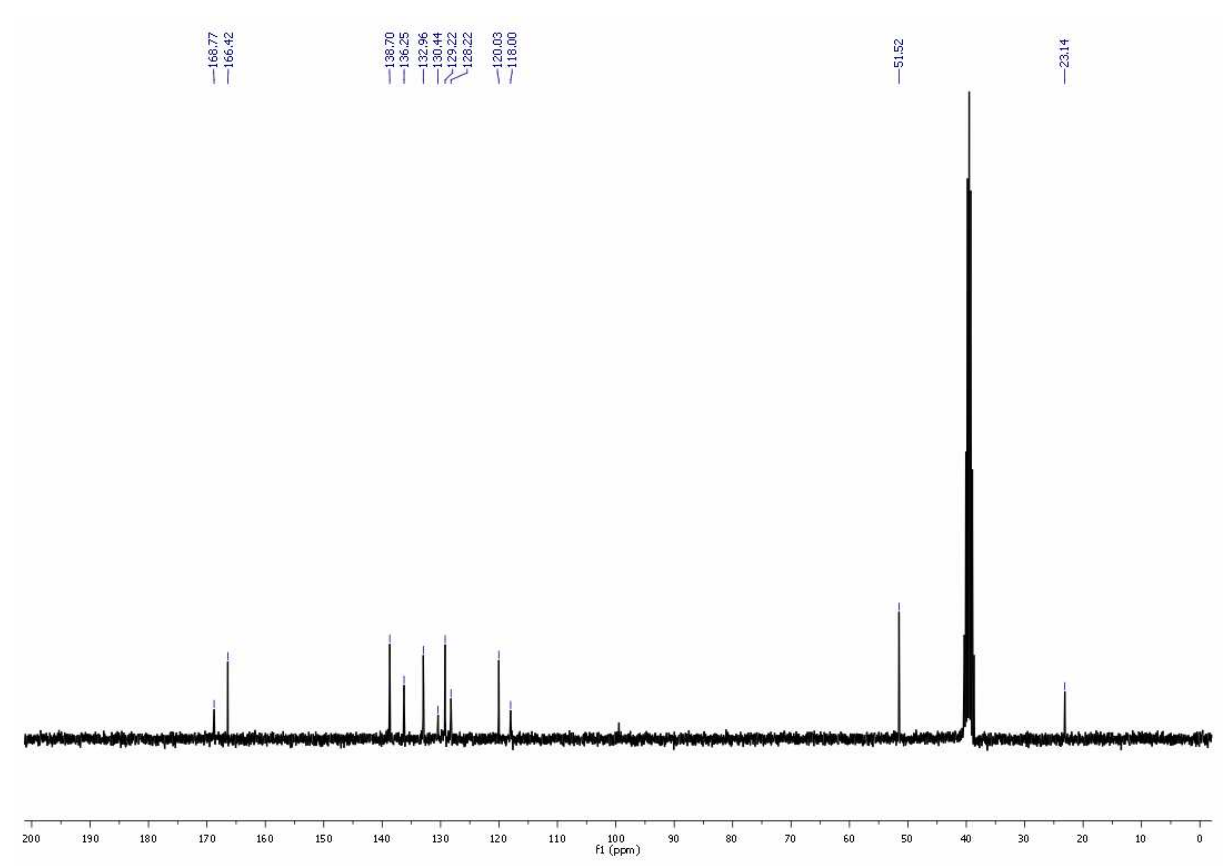
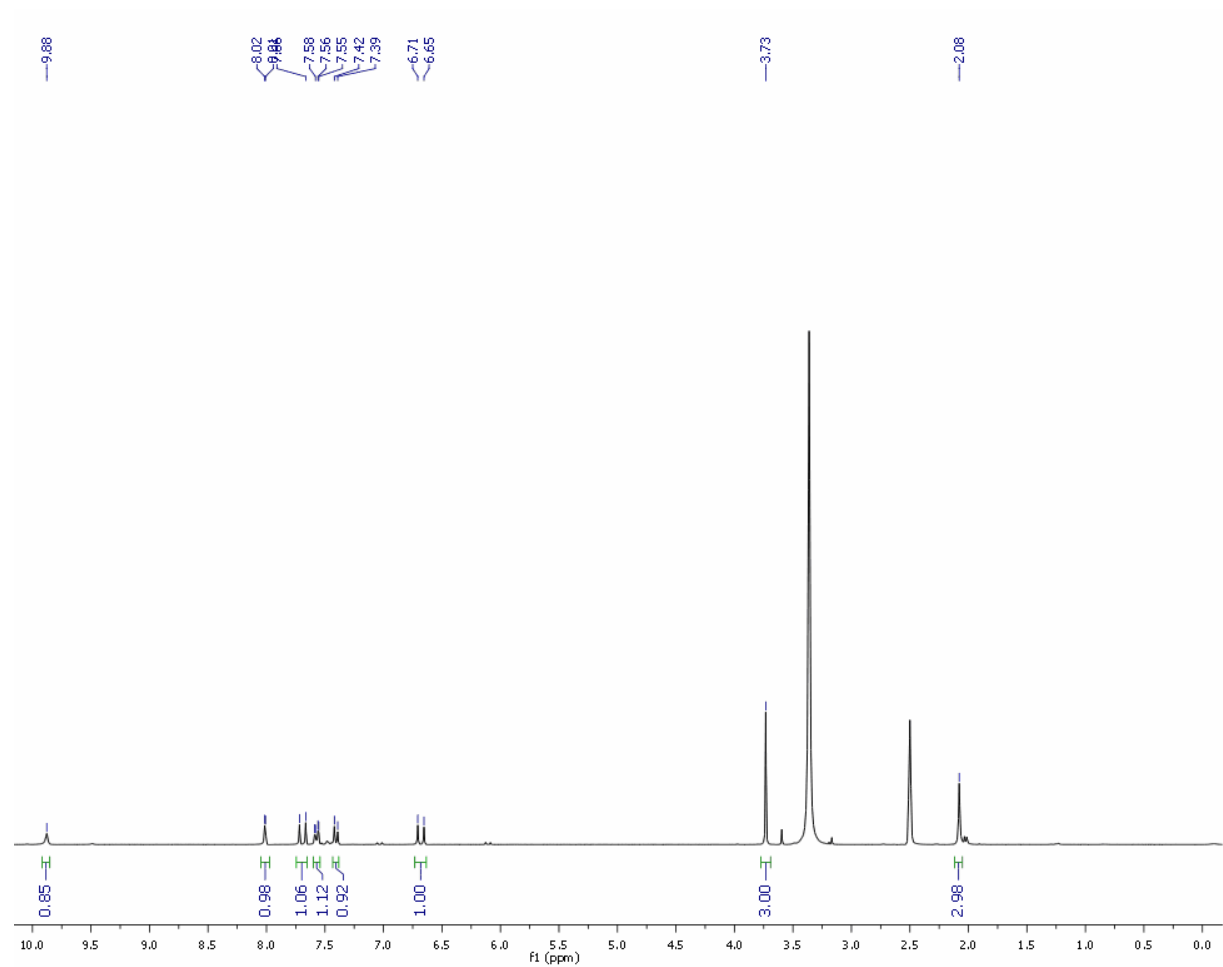


(*E*)-Methyl 3-(2-acetamido-5-bromophenyl)acrylate (**2e**)

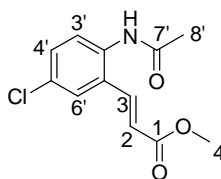


Following the general procedure (method A), (*E*)-methyl 3-(2-acetamido-5-bromophenyl)acrylate (**2e**) was obtained from 4-bromoacetamide (**1e**) (0.5 mmol, 107 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane / ethyl acetate 2 : 1) to afford **2e** as a colourless solid (49 %, 0.25 mmol, 73 mg).

¹H NMR (300 MHz, DMSO) δ 9.88 (s, 1H, -NH), 8.01 (d, J = 2.1 Hz, 1H, 6'-H), 7.69 (d, J = 16.0 Hz, 1H, 3-H), 7.57 (dd, J = 2.2, 8.6 Hz, 1H, 4'-H), 7.41 (d, J = 8.6 Hz, 1H, 3'-H), 6.68 (d, J = 15.9 Hz, 1H, 2-H), 3.73 (s, 3H, 4-H), 2.08 (s, 3H, 8'-H). ¹³C NMR (75 MHz, DMSO) δ 168.8, 166.4, 136.3, 132.9, 130.4, 129.2, 128.2, 128.2, 120.1, 118.0, 51.5, 23.1. MS (EI) m/z = 299 (13 %), 257 (17 %), 226 (46 %), 197 (22 %), 43 (100 %). HRMS (EI) m/z calcd for C₁₂H₁₂BrNO₃ [M]⁺: 297.0001, found 296.9984. IR ν 3273 (w), 1713 (m), 1284 (m), 1030 (w), 863 (w). mp 188°C.



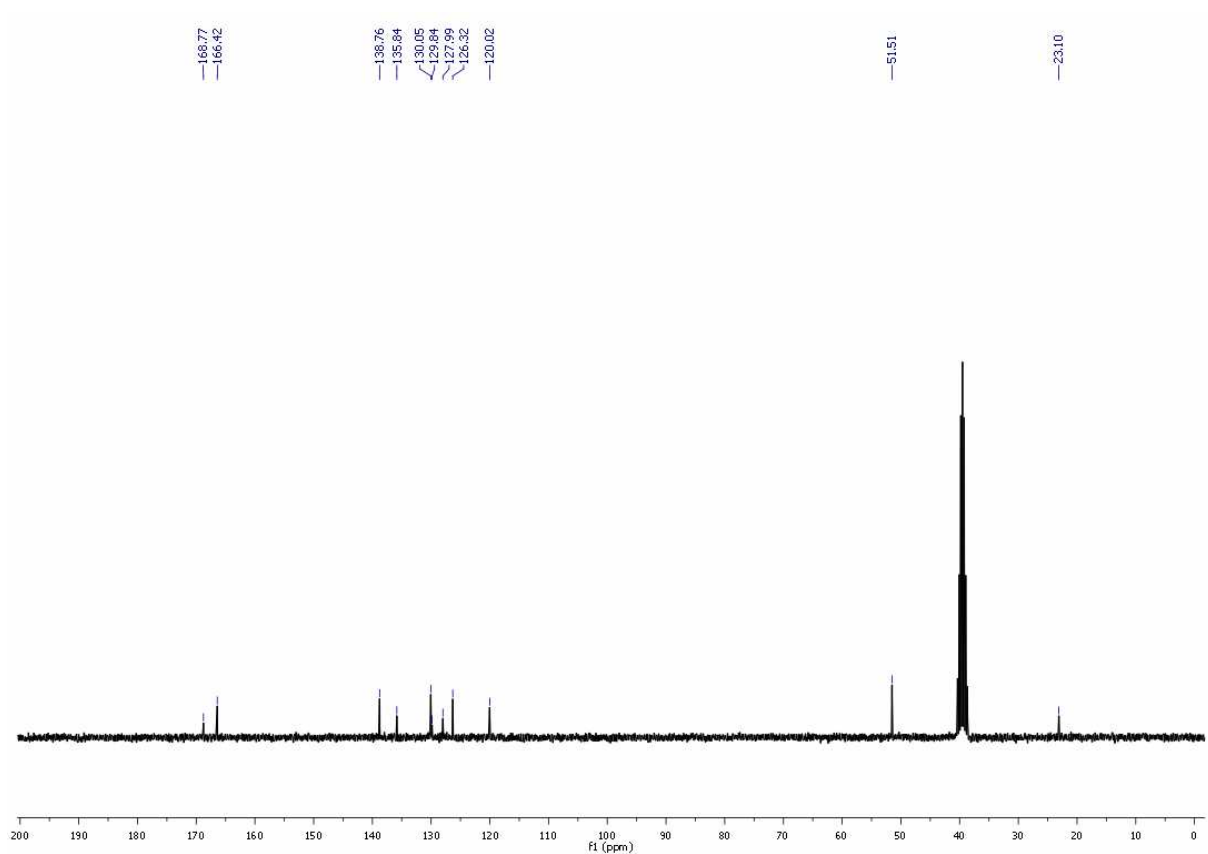
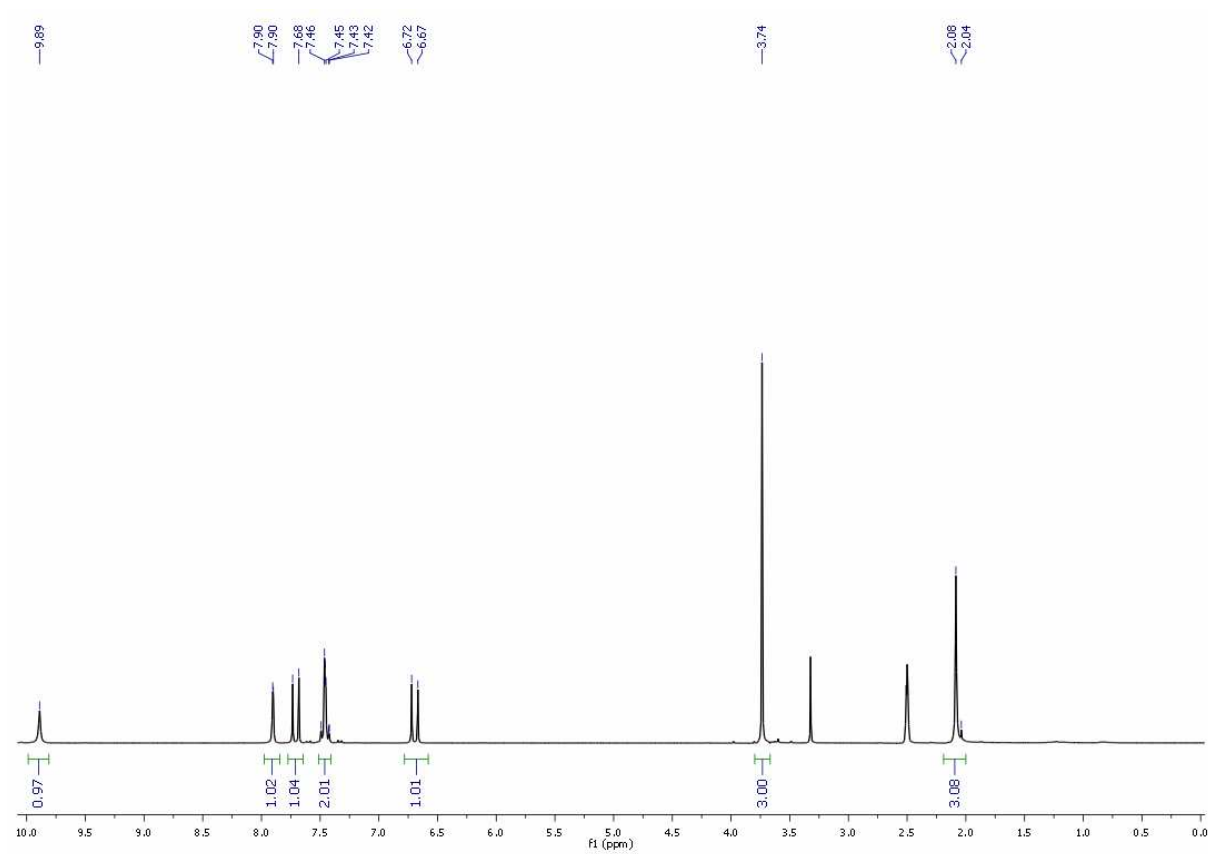
(*E*)-Methyl 3-(2-acetamido-5-chlorophenyl)acrylate (**2f**)



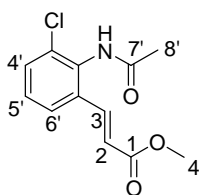
Following the general procedure (method A), (*E*)-methyl 3-(2-acetamido-5-chlorophenyl)acrylate (**2f**) was obtained from 4-chloroacetamide (**1f**) (1.0 mmol, 169 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane / ethyl acetate 2 : 1) to afford **2f** as a colourless solid (73 %, 0.73 mmol, 185 mg).

¹H NMR (300 MHz, DMSO) δ 9.89 (s, 1H, -NH), 7.90 (d J = 1.7 Hz, 1H, 6'-H), 7.71 (d, J = 16.0 Hz, 1H, 3-H), 7.51-7.41 (2H, 3'-H, 4'-H), 6.69 (d, J = 16.0 Hz, 1H, 2-H), 3.74 (s, 3H, 4-H), 2.06 (s, 3H, 8'-H). ¹³C NMR (75 MHz, DMSO) δ 168.8, 166.4, 138.8, 135.8, 130.0, 129.8, 127.9, 126.3, 120.0, 51.5, 23.1. MS (EI) m/z = 253 (24 %), 211 (29 %), 180 (100 %), 151 (50 %), 43 (55 %). HRMS (EI) m/z calcd for C₁₂H₁₂ClNO₃ [M]⁺: 253.0506, found 253.0505. Anal. calcd for C₁₂H₁₂ClNO₃: C, 56.8 %; H, 4.8 %; N, 5.5 %, found C, 57.3 %; H, 4.8 %; N, 5.4 %. IR ν 3261 (m), 1719 (s), 1522 (s), 1168 (s), 896 (w). mp 181°C (Lit.³: 172-174°C).

³ Nippon Kayaku Kabushiki Kaisha, Patent US4997972A1 1991.

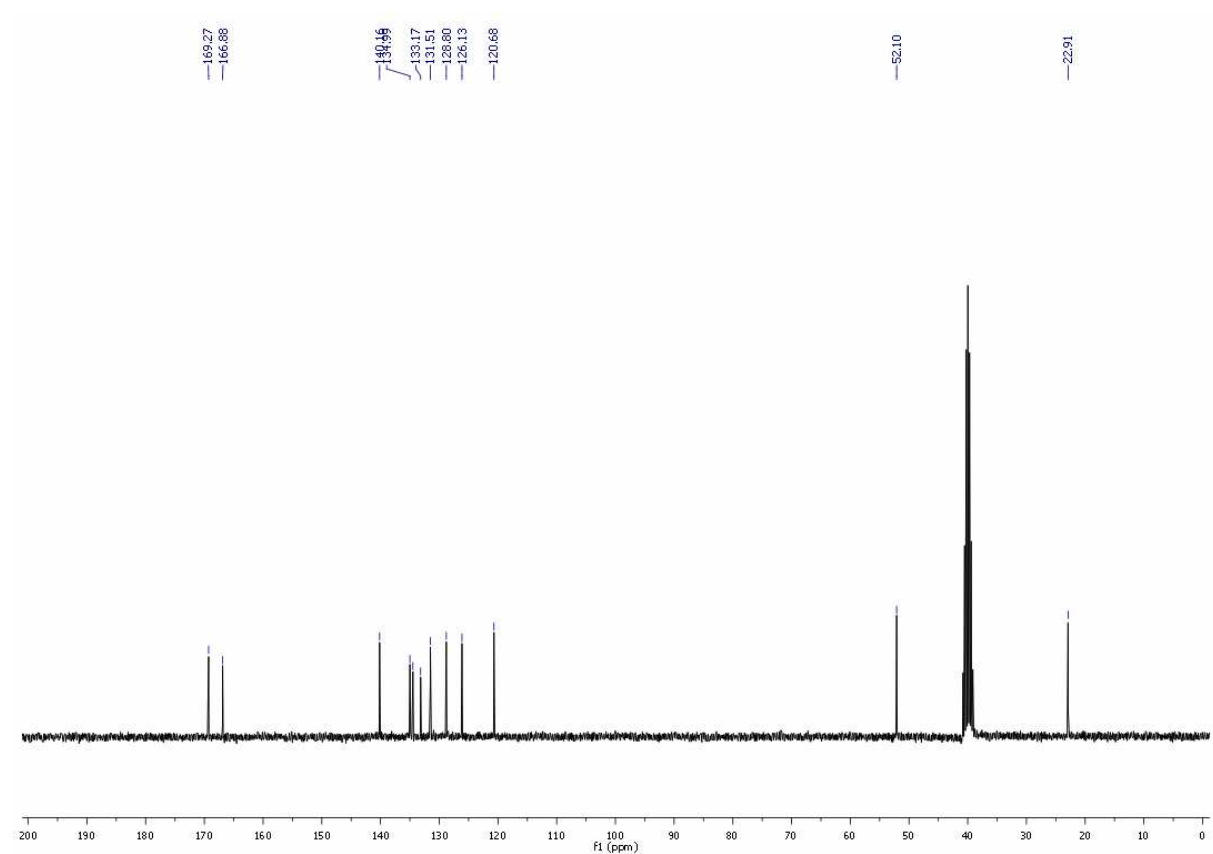
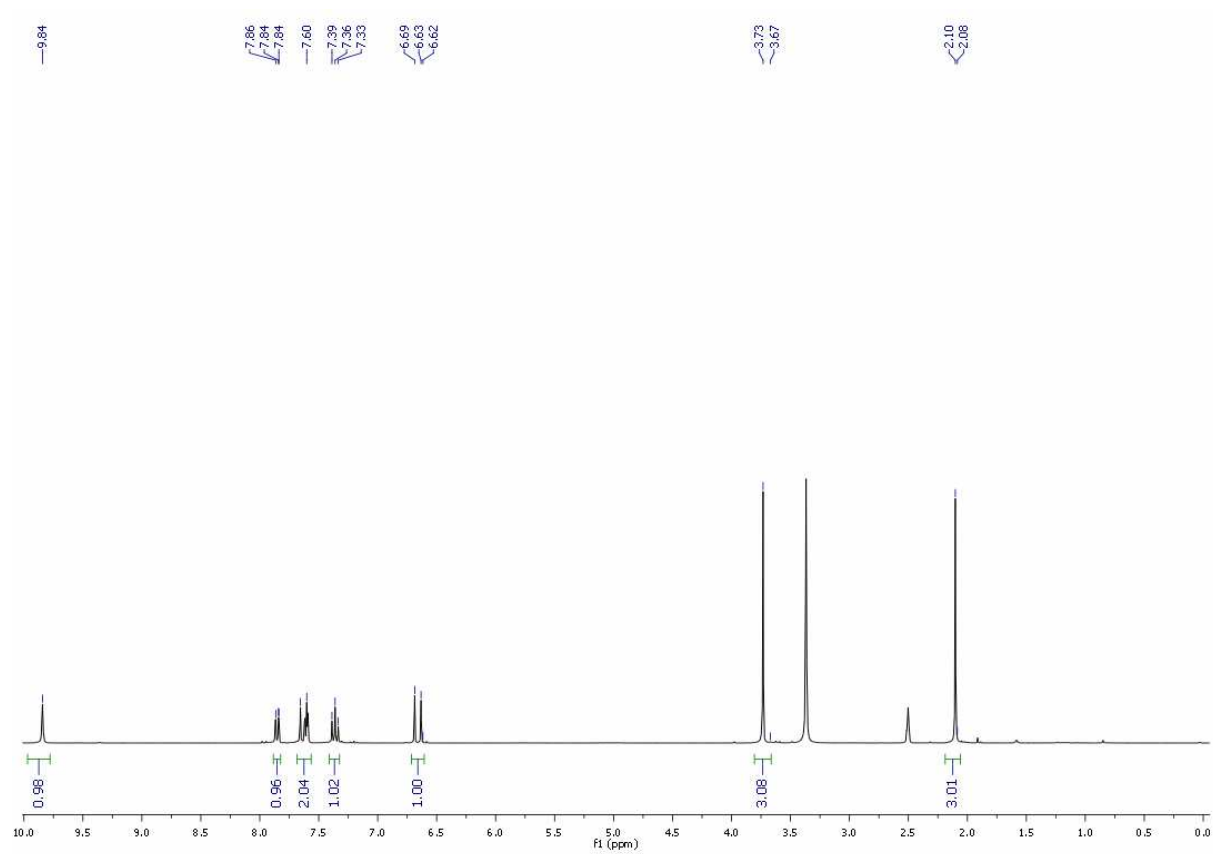


(*E*)-Methyl 3-(2-acetamido-3-chlorophenyl)acrylate (**2g**)

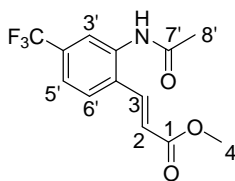


Following the general procedure (method A), (*E*)-methyl 3-(2-acetamido-3-chlorophenyl)acrylate (**2g**) was obtained from 2-chloroacetamide (**1g**) (1.0 mmol, 169 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane / ethyl acetate 2 : 1) to afford **2g** as a colourless solid (40 %, 0.40 mol, 102 mg).

¹H NMR (300 MHz, DMSO) δ 9.84 (s, 1H, -NH), 7.85 (dd, J = 1.0, 7.9 Hz, 1H, 6'-H), 7.63 (d, J = 16.0 Hz, 1H, 3-H), 7.61 (dd, J = 1.1, 7.9 Hz, 1H, 4'-H), 7.36 (t, J = 8.0 Hz, 1H, 5'-H), 6.66 (d, J = 16.1 Hz, 1H, 2-H), 3.73 (s, 3H, 4-H), 2.10 (s, 3H, 8'-H). **¹³C NMR (75 MHz, DMSO)** δ 169.3, 166.9, 140.2, 134.9, 134.5, 133.2, 131.5, 128.8, 126.1, 120.7, 52.1, 22.9. **MS (EI)** m/z = 253 (13 %), 180 (17 %), 151 (13 %), 89 (13 %), 43 (100 %). **HRMS (EI)** m/z calcd for C₁₂H₁₂ClNO₃ [M]⁺: 253.0506, found 253.0495. **Anal.** calcd for C₁₂H₁₂ClNO₃: C, 56.8 %; H, 4.8 %; N, 5.5 %, found C, 57.0 %; H, 4.6 %; N, 5.5 %. **IR**, ν 3238(w), 1716 (m), 1455 (w), 1281 (m), 791 (w). **mp** 158-165°C.

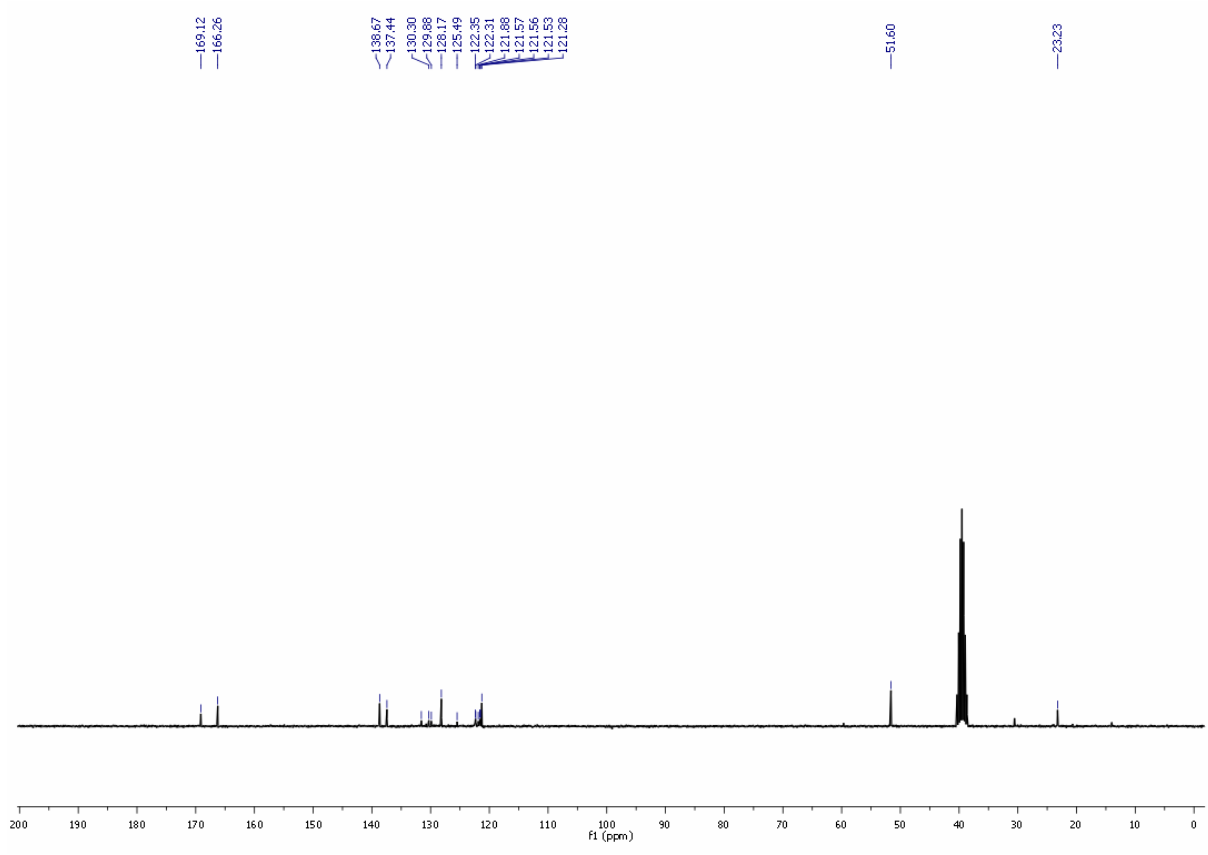
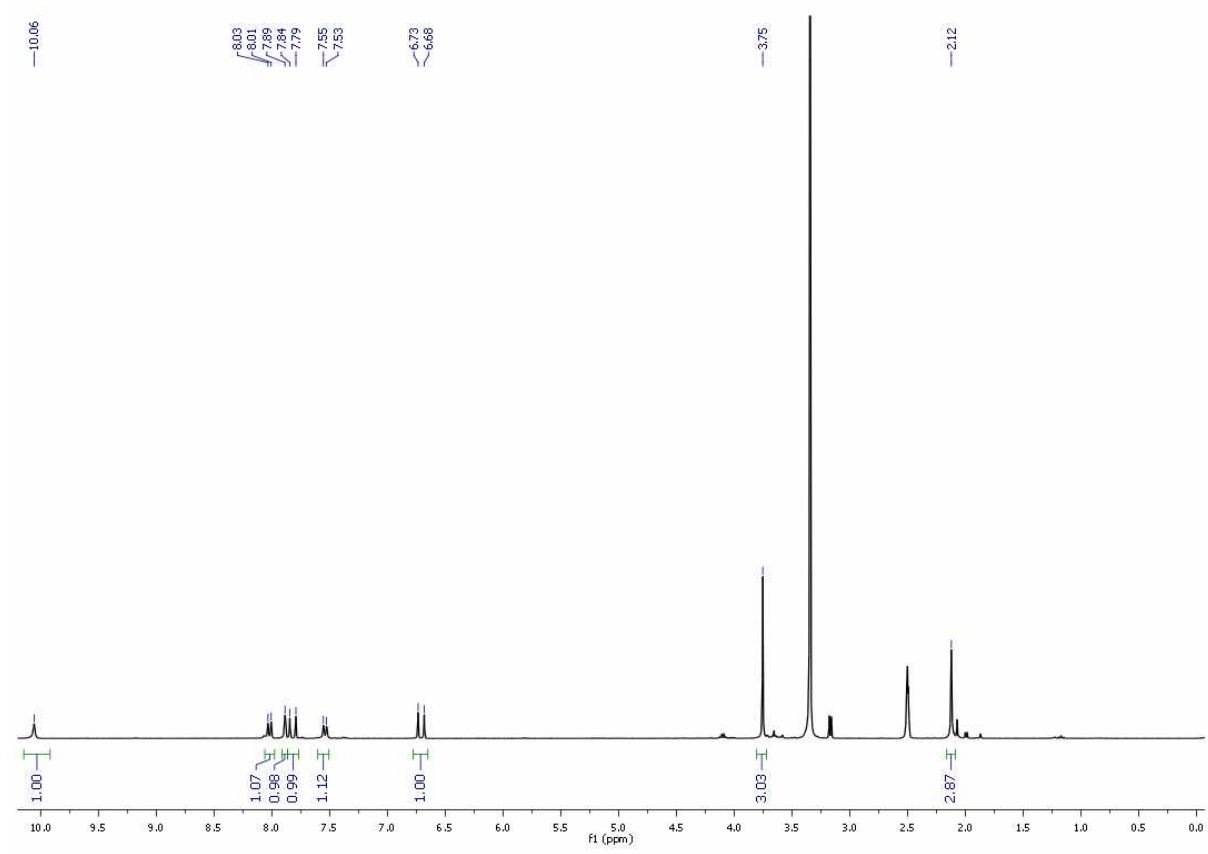


(*E*)-Methyl 3-(2-acetamido-4-(trifluoromethyl)phenyl)acrylate (**2h**)

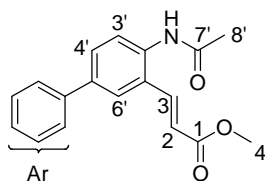


Following the general procedure (method A), (*E*)-methyl 3-(2-acetamido-4-(trifluoromethyl)phenyl)acrylate (**2h**) was obtained from 3-trifluoromethylacetamide (**1h**) (1.0 mmol, 203 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane / ethyl acetate 1 : 1) to afford **2h** as a colourless solid (72 %, 0.72 mol, 207 g).

¹H NMR (300 MHz, DMSO) δ 10.06 (s, 1H, -NH), 8.02 (d, J = 8.3 Hz, 1H, 6'-H), 7.89 (s, 1H, 3'-H), 7.82 (d, J = 15.9 Hz, 1H, 3-H), 7.54 (d, J = 8.2 Hz, 1H, 5'-H), 6.71 (d, J = 15.9 Hz, 1H, 2-H), 3.03 (s, 3H, 4-H), 2.87 (s, 3H, 8'-H). **¹³C NMR (75 MHz, DMSO)** δ 169.1, 166.3, 138.7, 137.4, 131.6, 130.1 (q, 2J = 31.5 Hz), 128.2, 123.7 (q, 1J = 270.1 Hz), 122.3 (q, 3J = 3.0 Hz), 121.55 (q, 3J = 3.0 Hz), 121.3, 51.6, 23.2. **MS (EI)** m/z = 287 (13 %), 214 (54 %), 161 (100 %), 43 (100 %). **HRMS (EI)** m/z calcd for C₁₃H₁₂F₃NO₃ [M]⁺: 287.0769, found 287.0761. **IR**, ν 3254 (m), 2950 (m), 1663 (s), 1193 (s), 1169 (s). **mp** 148-149°C.

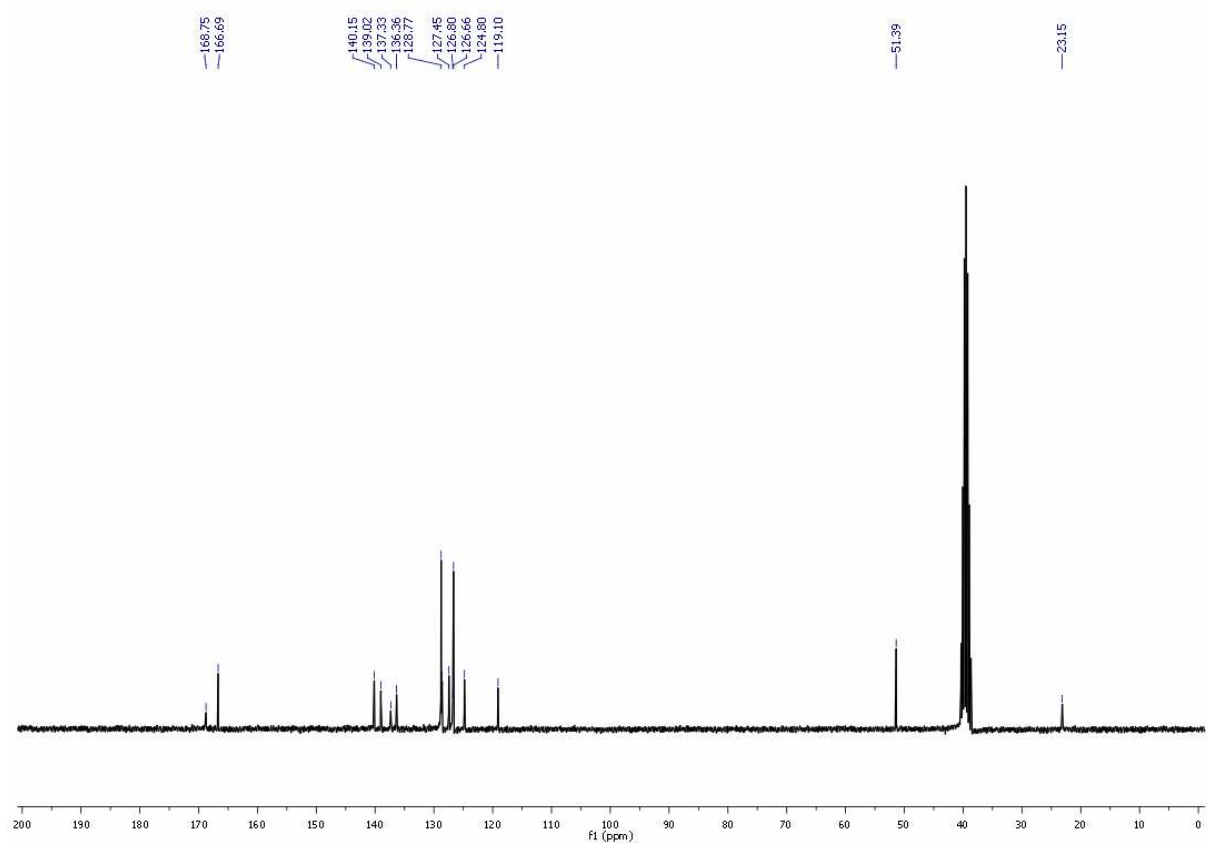
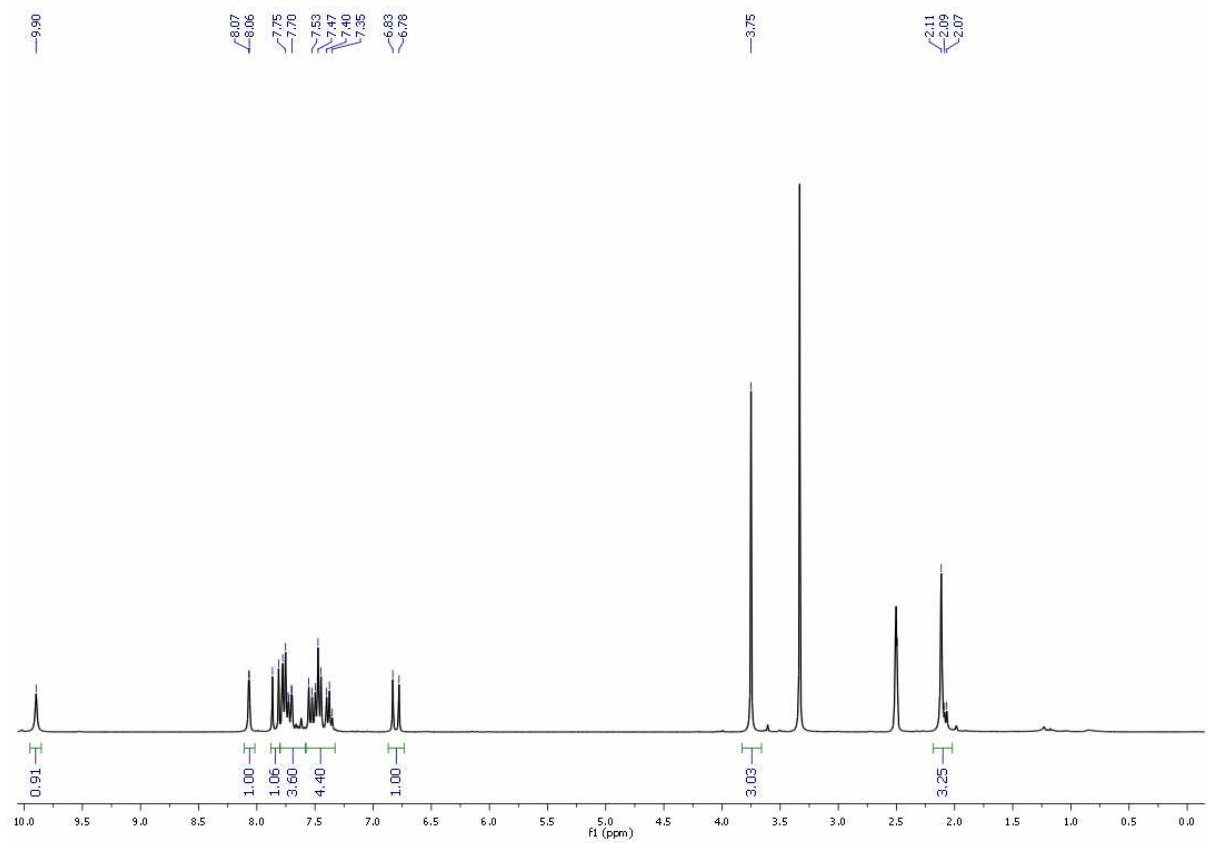


(*E*)-Methyl 3-(4-acetamidobiphenyl-3-yl)acrylate (**2i**)



Following the general procedure (method A), (*E*)-methyl 3-(4-acetamido-3-yl)acrylate (**2i**) was obtained from *N*-(biphenyl-4-yl)acetamide (**1d**) (1.0 mmol, 211 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane / ethyl acetate 3 : 1) to afford **2d** as a colourless solid (60 %, 0.60 mmol, 176 mg).

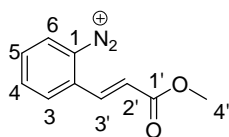
¹H NMR (300 MHz, DMSO) δ 9.90 (s, 1H, -NH), 8.07 (d, J = 1.8 Hz, 1H, 6'-H), 7.84 (d, J = 16.0 Hz, 1H, 3-H), 7.76 (d, J = 7.2 Hz, 1H, 3'-H), 7.71 (d, J = 1.9, 8.4 Hz, 1H, 3'-H), 7.80-7.75 (m, 1H, Ar-H), 7.6-7.4 (4H, Ar-H), 6.80 (d, J = 15.9 Hz, 1H, 2-H), 3.75 (s, 3H, 4-H), 2.09 (s, 3H, 8'-H). **¹³C NMR (75 MHz, DMSO)** δ 168.8, 166.7, 140.2, 139.0, 137.3, 136.4, 128.8, 128.6, 127.5, 126.8, 126.7, 124.8, 119.1. **MS (EI)** m/z = 295 (58 %), 253 (22 %), 222 (100 %), 193 (38 %), 165 (28 %). **HRMS (EI)** m/z calcd for C₁₈H₁₇NO₃ [M]⁺: 295.1216, found 295.1208. **Anal.** calcd for C₁₈H₁₇NO₃: C, 73.2 %; H, 5.8 %; N, 4.7 %, found C, 72.9 %; H, 5.6 %; N, 5.0 %. **IR** ν 3273 (w), 1718 (s), 1660 (s), 1294 (m), 1168 (s). **mp** 195-200°C.



General procedure for the synthesis of diazonium salts:

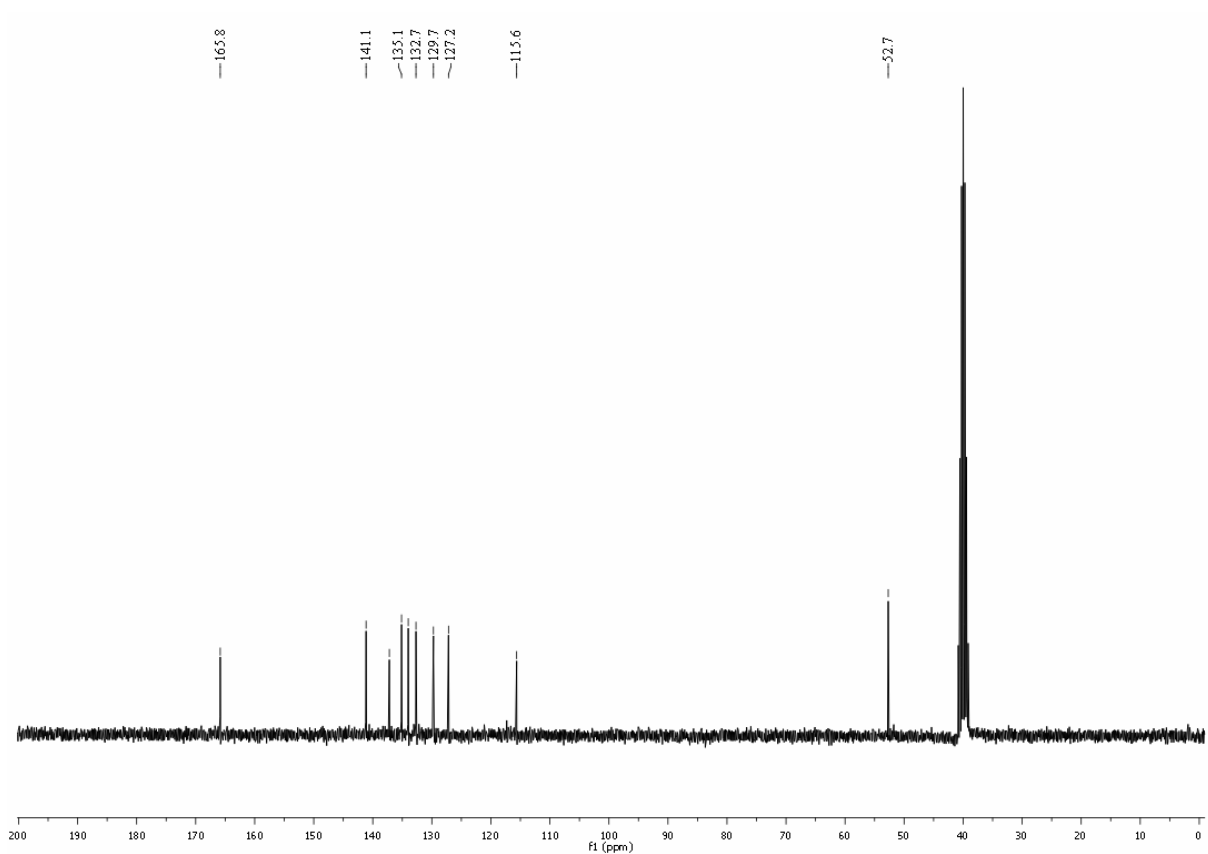
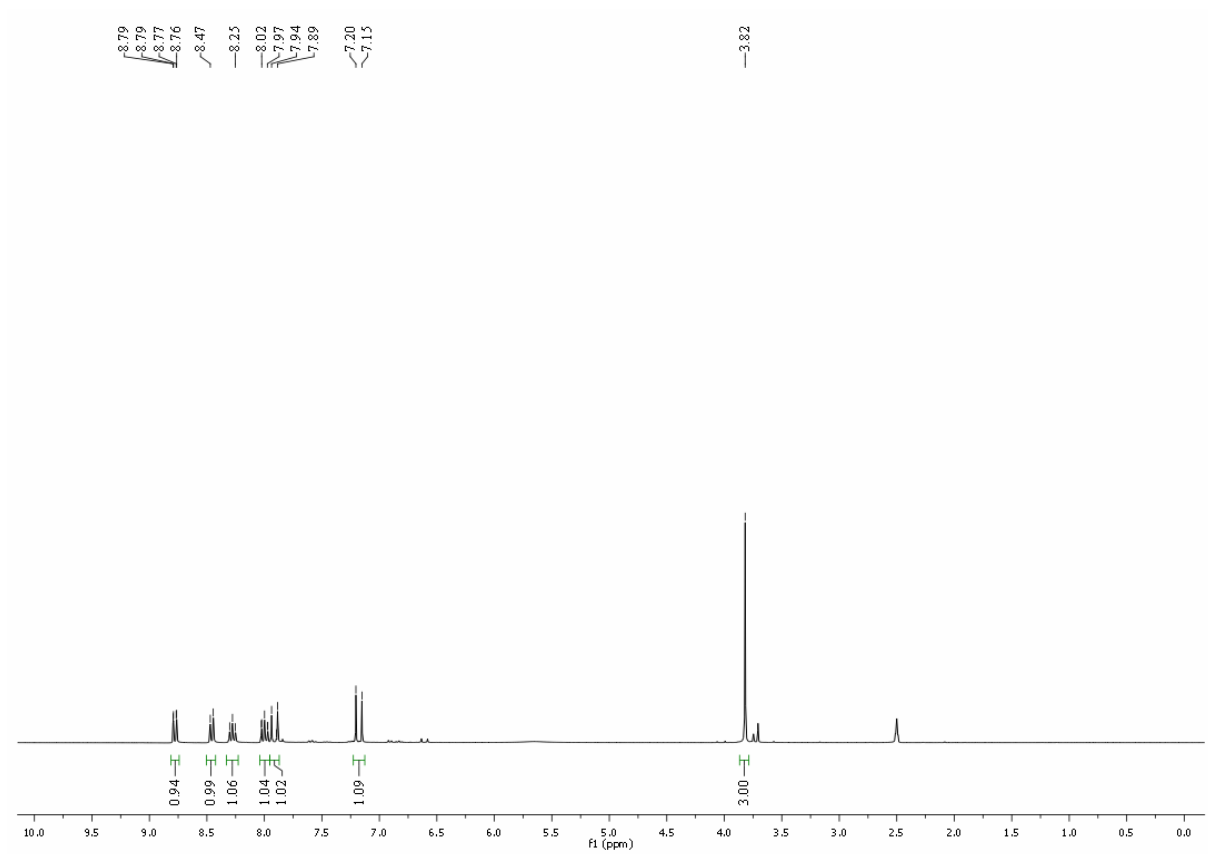
To a solution of compound **2** (1.0 mmol) in dry methanol (6 mL) was added $\text{BF}_3 \cdot \text{MeOH}$ (3.0 mmol, 324 μL). The solution was stirred for 16 h at 70°C. The reaction was cooled to 0°C. *tert*-Butylnitrite (1.0 mmol, 120 μL) was added. After the diazonium salt precipitated, the reaction mixture was stirred 30 min. The precipitate was filtered through a Büchner funnel and washed with a small amount of cold methyl *tert*-butyl ether.

(*E*)- 2-(3-Methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (**3a**)

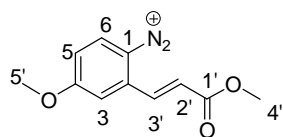


Following the general procedure, (*E*)-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (**3a**) was obtained from (*E*)-methyl 3-(2-acetamidophenyl)acrylate (**2a**) (0.5 mmol, 110 mg) as a colourless beige-coloured solid (76 %, 0.38 mmol, 105 mg).

¹H NMR (300 MHz, DMSO) δ 8.78 (d, J = 3.3 Hz, 1H, 6-H), 8.46 (d, J = 7.8 Hz, 1H, 3-H), 8.28 (t, J = 7.5 Hz, 1H, 5/4-H), 8.0 (t, J = 7.9 Hz, 1H, 4/5-H), 7.91 (d, J = 16.3 Hz, 1H, 1'-H), 7.18 (d, J = 15.7 Hz, 1H, 2'-H), 3.82 (s, 3H, 4'-H), 2.05 (s, 3H, 8'-H) **¹³C NMR (75 MHz, DMSO)** δ 165.8, 141.1, 137.2, 135.1, 134.0, 132.7, 129.7, 127.2, 115.6, 52.7. **MS (EI)** m/z = 180 (55 %), 149 (100 %), 121 (31 %), 101 (30 %). **HRMS (ESI)** m/z calcd for C₁₀H₉N₂O₂ [M]⁺: 189.0664, found 189.0771. **IR**, ν 3360 (m), 2230 (m), 1700 (s), 1590 (s), 1304 (s).

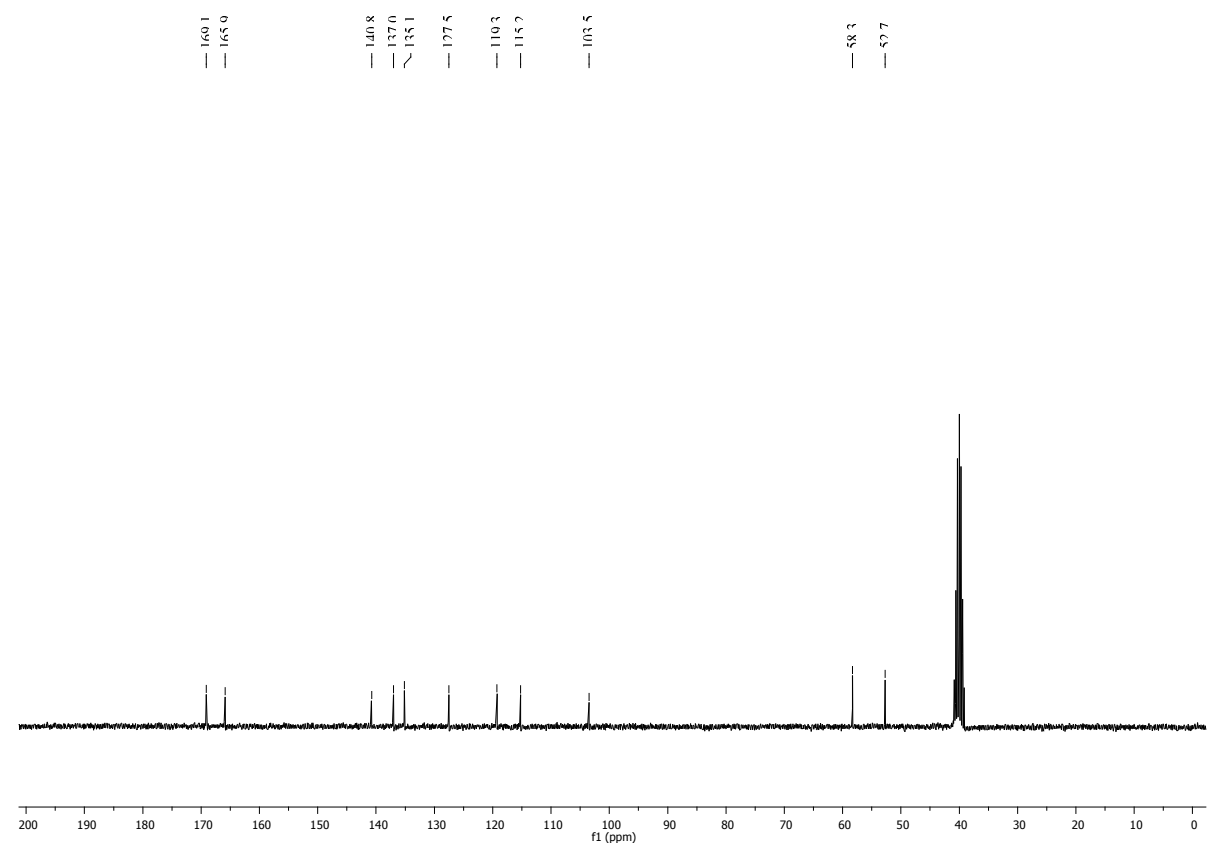
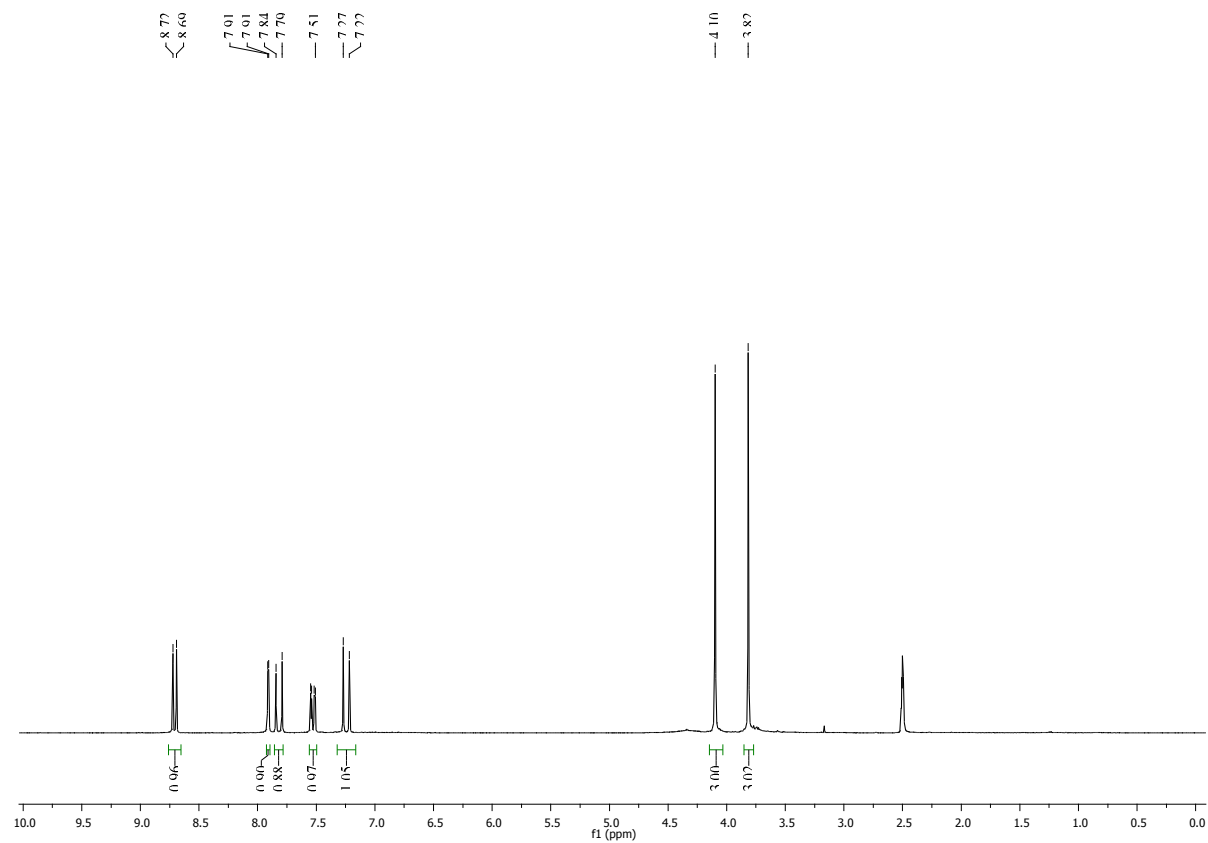


(*E*)-4-Methoxy-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (**3b**)

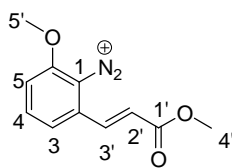


Following the general procedure, (*E*)-4-methoxy-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (**3b**) was obtained from (*E*)-methyl 3-(2-acetamido-5-methoxyphenyl)acrylate (**2b**) (10.0 mmol, 2.50 g) as a beige-coloured solid (94 %, 9.5 mmol, 2.90 g).

¹H NMR (300 MHz, DMSO) δ 8.71 (d, J = 9.3 Hz, 1H, 6-H), 7.91 (d, J = 2.5 Hz, 1H, 3-H), 7.82 (d, J = 15.8 Hz, 1H, 1'-H), 7.53 (dd, J = 2.5, 9.3 Hz, 1H, 5-H), 7.24 (d, J = 15.7 Hz, 1H, 2'-H), 4.10 (s, 3H, 5'-H), 3.82 (s, 3H, 4'-H). **¹³C NMR (75 MHz, DMSO)** δ 169.1, 165.9, 140.8, 137.0, 135.1, 127.5, 119.3, 115.2, 103.5, 58.3, 52.7. **MS (EI)** m/z = 210 (59 %), 179 (58 %), 136 (24 %), 211 (13 %). **HRMS (ESI)** m/z calcd for C₁₁H₁₁N₂O₃ [M]⁺: 219.0770, found 219.0875. **IR**, ν 2959 (m), 2251 (m), 1714 (s), 1560 (s), 1311 (s).

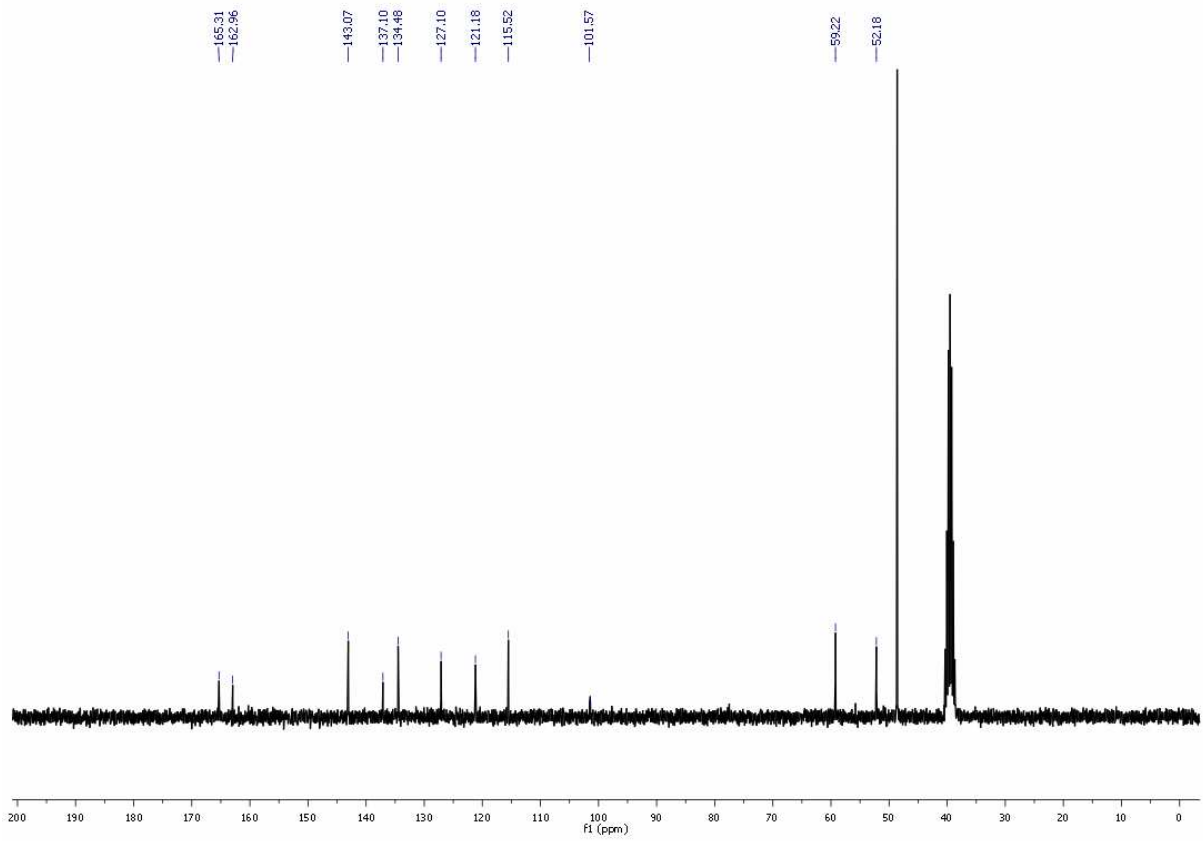
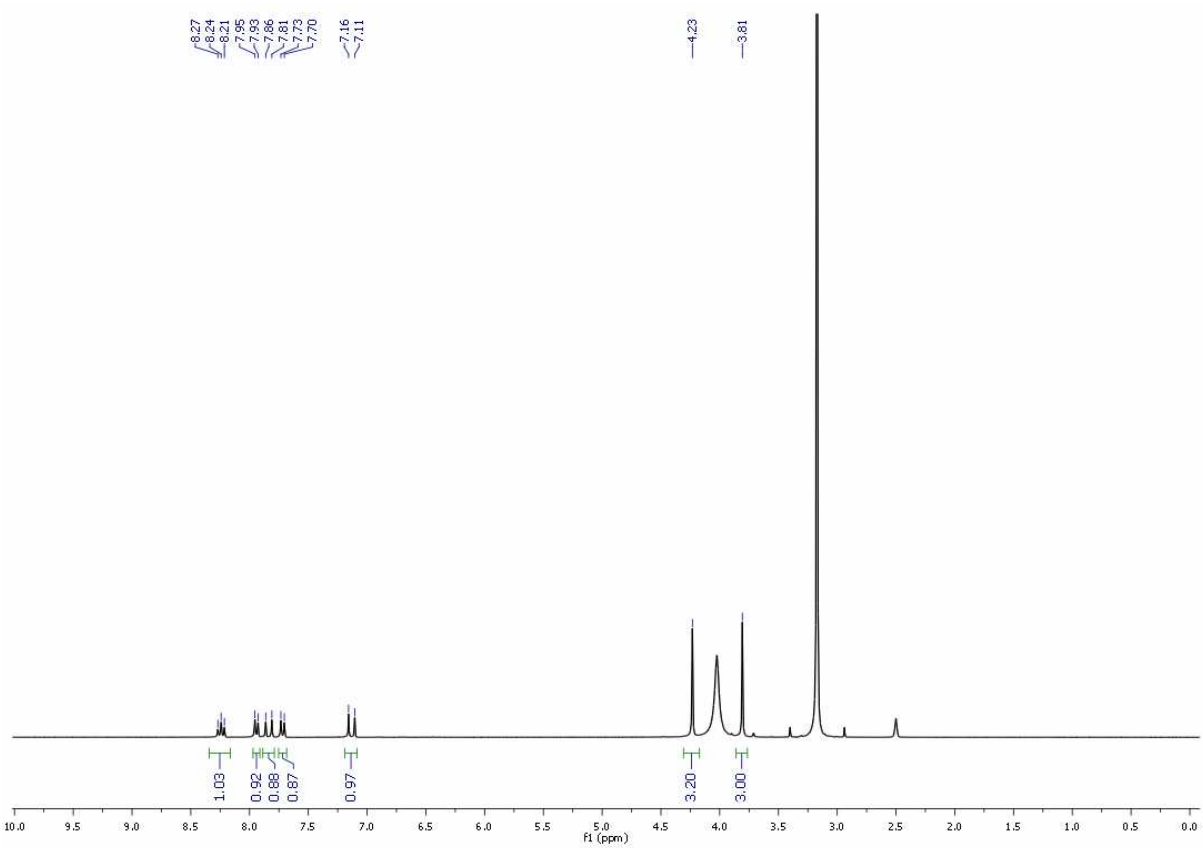


(E)-6-Methoxy-2-(3-Methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (3c)

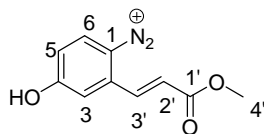


Following the general procedure, **(E)-6-methoxy-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (3c)** was obtained from (*E*)-methyl 3-(2-acetamido-3-methoxyphenyl)acrylate (**2c**) (2.0 mmol, 498 mg) as a beige-coloured solid (65 %, 1.3 mmol, 400 mg).

¹H NMR (300 MHz, DMSO) δ 8.24 (t, J = 8.3 Hz, 1H, 4-H), 7.89 (d, J = 7.9 Hz, 1H, 5/3-H), 7.84 (d, J = 15.8 Hz, 1H, 1'-H), 7.72 (d, J = 8.8 Hz, 1H, 3/5-H), 7.13 (d, J = 15.7 Hz, 1H, 2'-H), 4.23 (s, 3H, 6'-H), 3.81 (s, 3H, 4'-H). **¹³C NMR (75 MHz, DMSO)** δ 165.3, 162.9, 143.1, 137.1, 134.5, 127.1, 121.2, 115.5, 101.6, 59.2, 52.2. **HRMS (ESI)** m/z calcd for C₁₁H₁₁N₂O₃ [M]⁺: 219.0770, found 219.0785. **IR** ν 3380 (m), 2255 (s), 1725 (s), 1639 (s), 1491 (s).

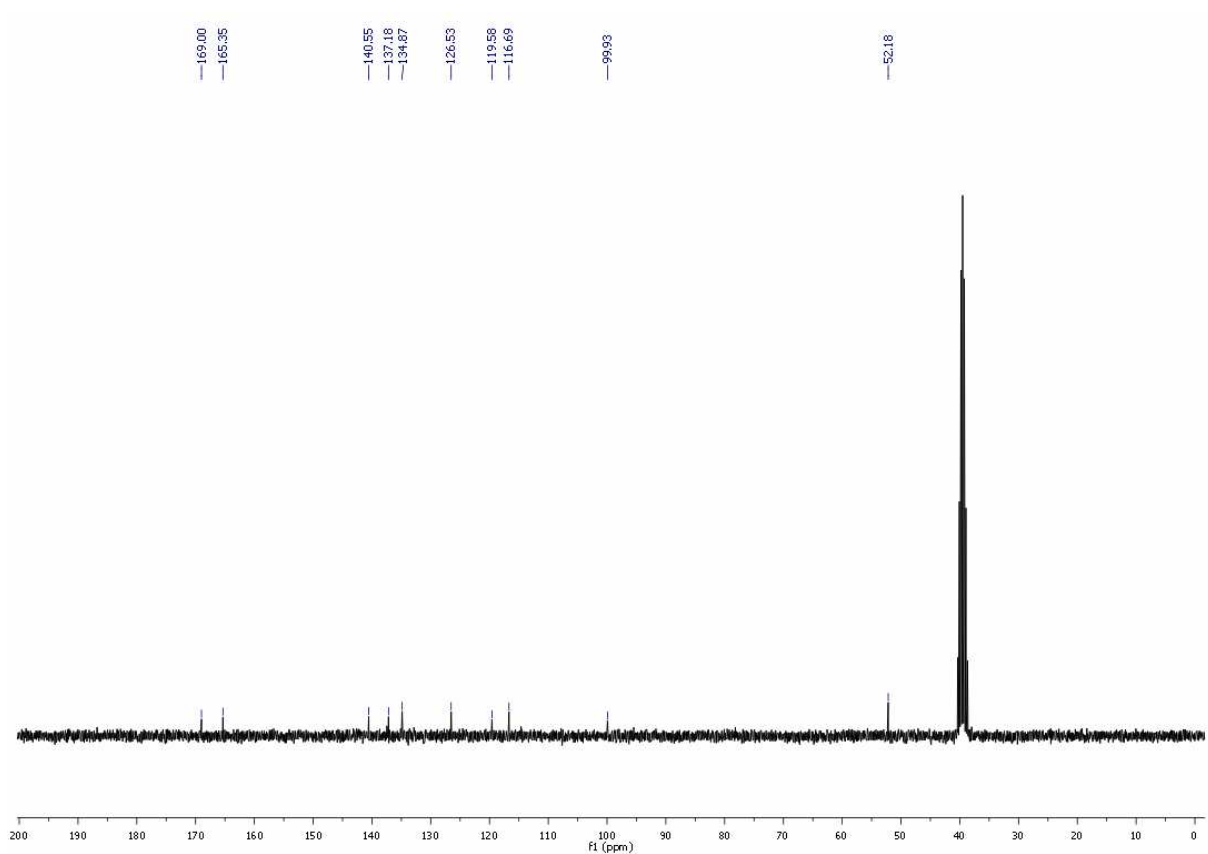
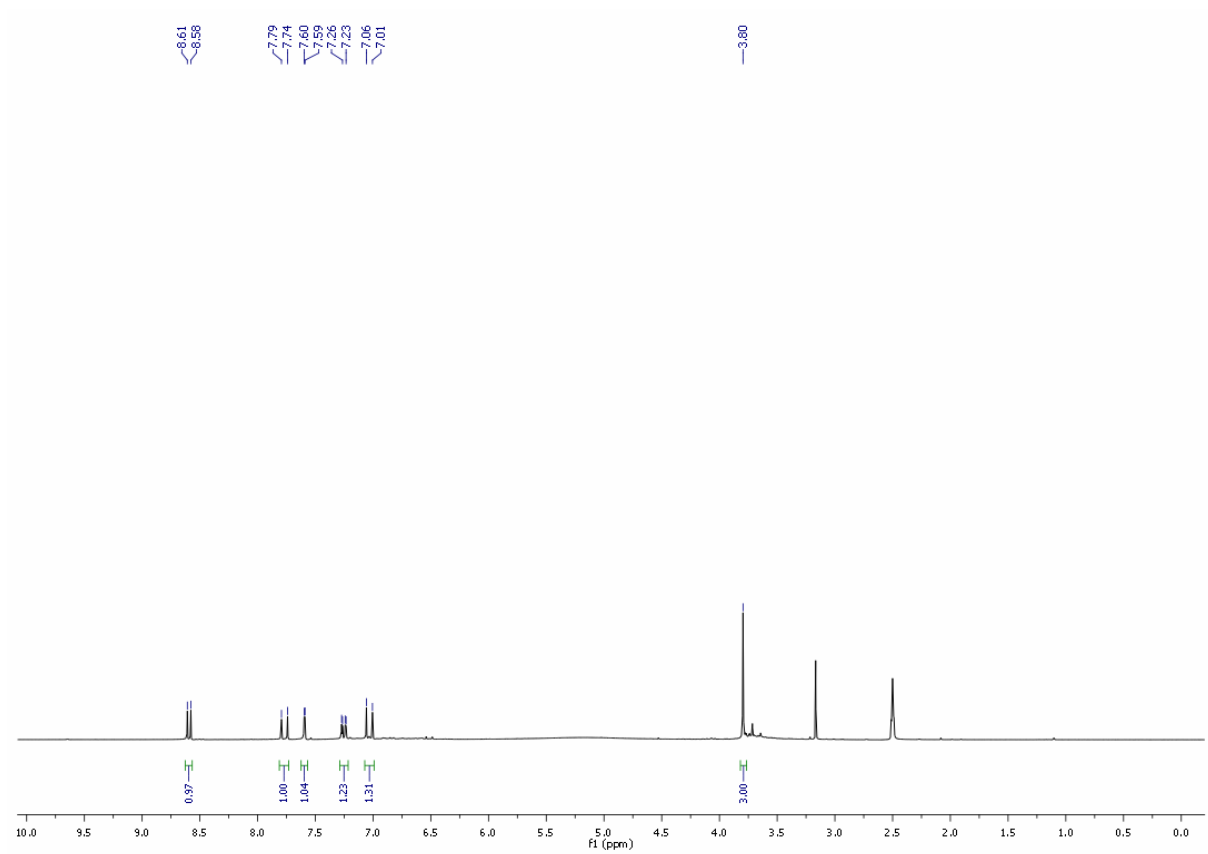


(E)-4-Hydroxy-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (3d)

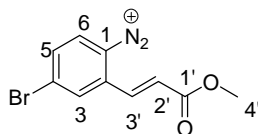


Following the general procedure, **(E)-4-hydroxy-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (3d)** was obtained from *(E)*-methyl 3-(2-acetamido-5-hydroxyphenyl)acrylate (**2d**) (2.7 mmol, 630 mg) as a beige-coloured solid (92 %, 2.5 mmol, 720 mg).

¹H NMR (300 MHz, DMSO) δ 8.59 (d, J = 9.2 Hz, 1H, 6-H), 7.77 (d, J = 15.9 Hz, 1H, 1'-H), 7.59 (d, J = 2.2 Hz, 1H, 3-H), 7.25 (dd, J = 2.3, 9.2 Hz, 1H, 5-H), 7.03 (d, J = 15.8 Hz, 1H, 2'-H), 3.82 (s, 3H, 4'-H). **¹³C NMR (75 MHz, DMSO)** δ 169.0, 165.4, 140.5, 137.2, 134.9, 126.5, 119.6, 116.7, 99.9, 52.2. **MS (EI)** m/z = 196 (62 %), 178 (72 %), 165 (83 %), 147 (100 %). **IR**, ν 3357 (m), 2231 (s), 1700 (s), 1631 (s), 1590 (s).

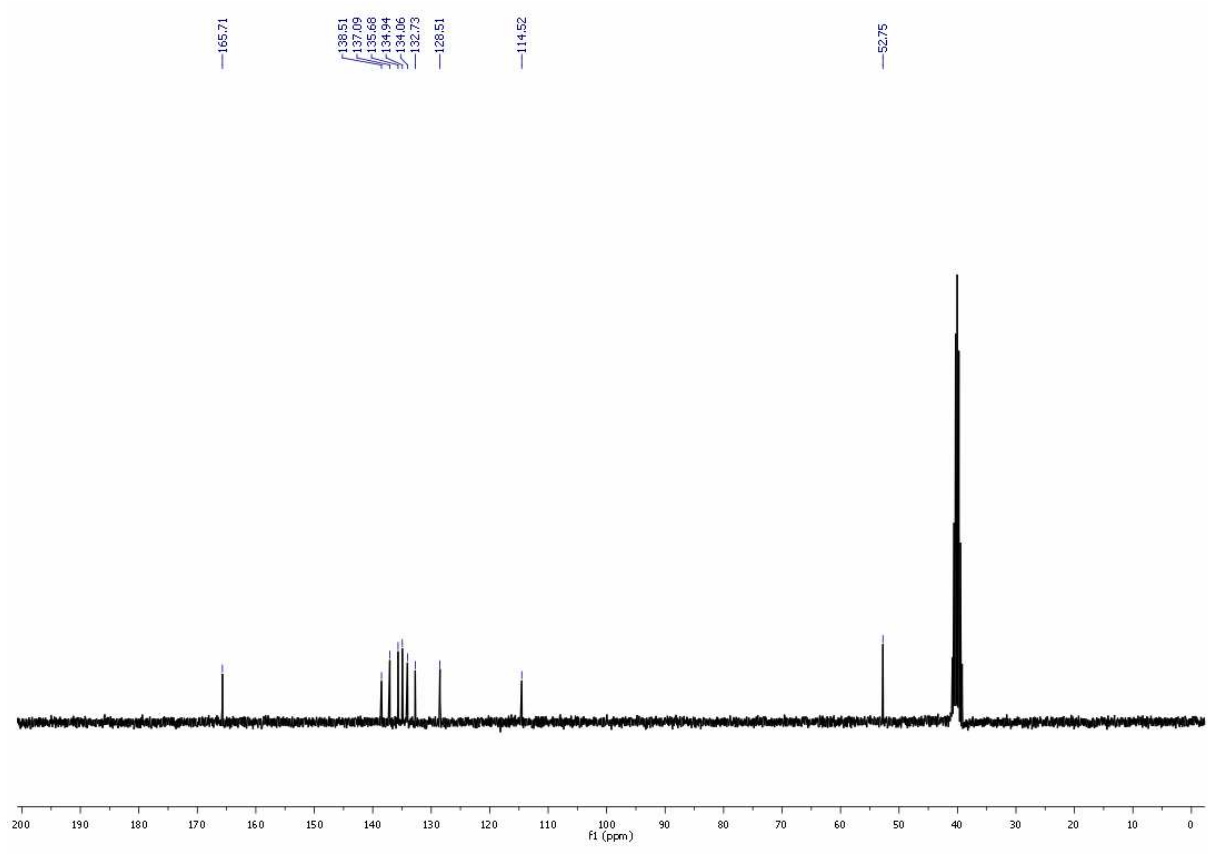
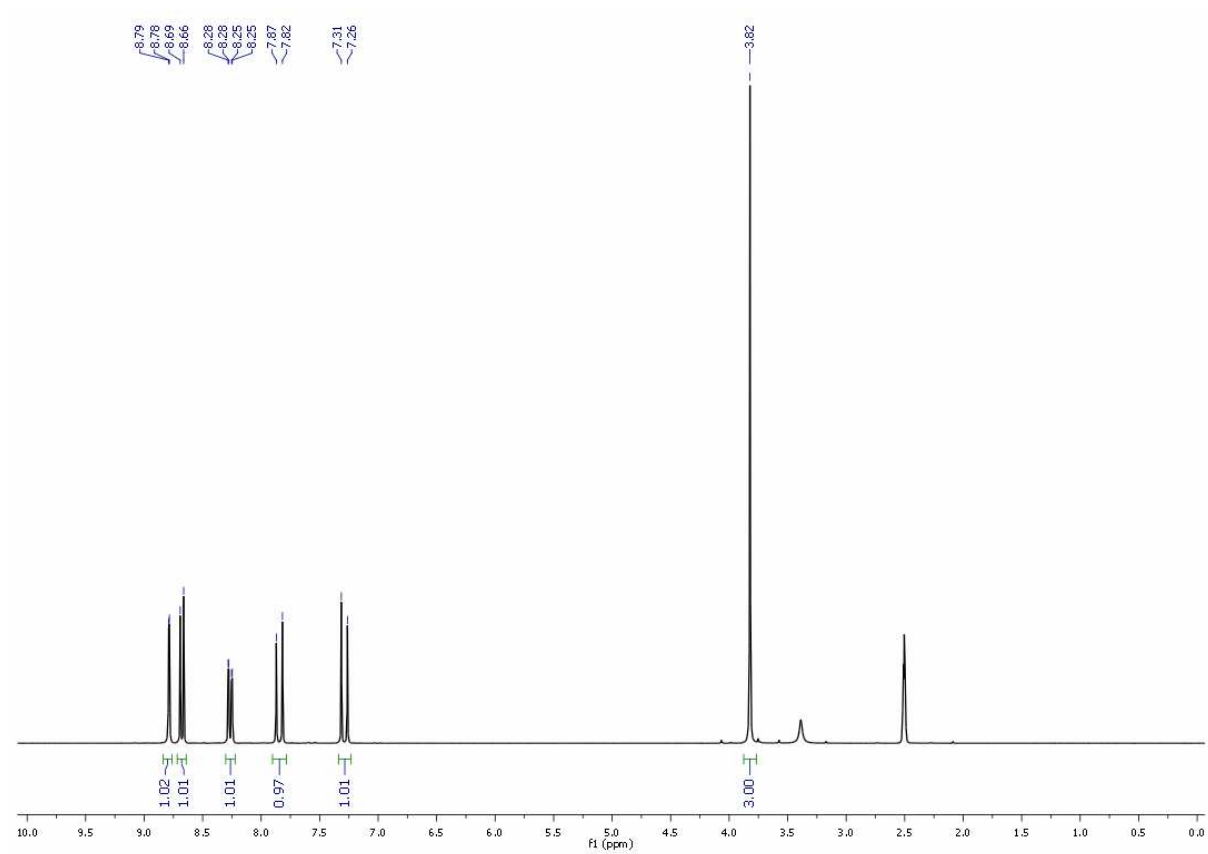


(*E*)-4-Bromo-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (**3e**)

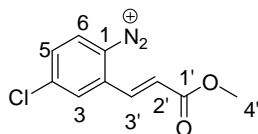


Following the general procedure, (*E*)-4-bromo-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (**3e**) was obtained from (*E*)-methyl 3-(2-acetamido-5-bromophenyl)acrylate (**2e**) (2.0 mmol, 596 mg) as a beige-coloured solid (70 %, 1.4 mmol, 506 mg).

¹H NMR (300 MHz, DMSO) δ 8.79 (d, *J* = 1.8 Hz, 1H, 3-H), 8.68 (d, *J* = 8.8 Hz, 1H, 6-H), 8.26 (dd, *J* = 1.9, 8.8 Hz, 1H, 5-H), 7.84 (d, *J* = 15.7 Hz, 1H, 1'-H), 7.29 (d, *J* = 15.7 Hz, 1H, 2'-H), 3.82 (s, 3H, 4'-H). ¹³C NMR (75 MHz, DMSO) δ 165.7, 138.5, 137.1, 135.7, 134.9, 137.1, 132.7, 128.5, 114.5, 52.8. HRMS (EI) *m/z* calcd for C₁₀H₈N₂O₂ [M]⁺: 266.9769, found 266.9796. IR ν 3440 (m), 2264 (s), 1715 (s), 1295 (s), 1186 (s).

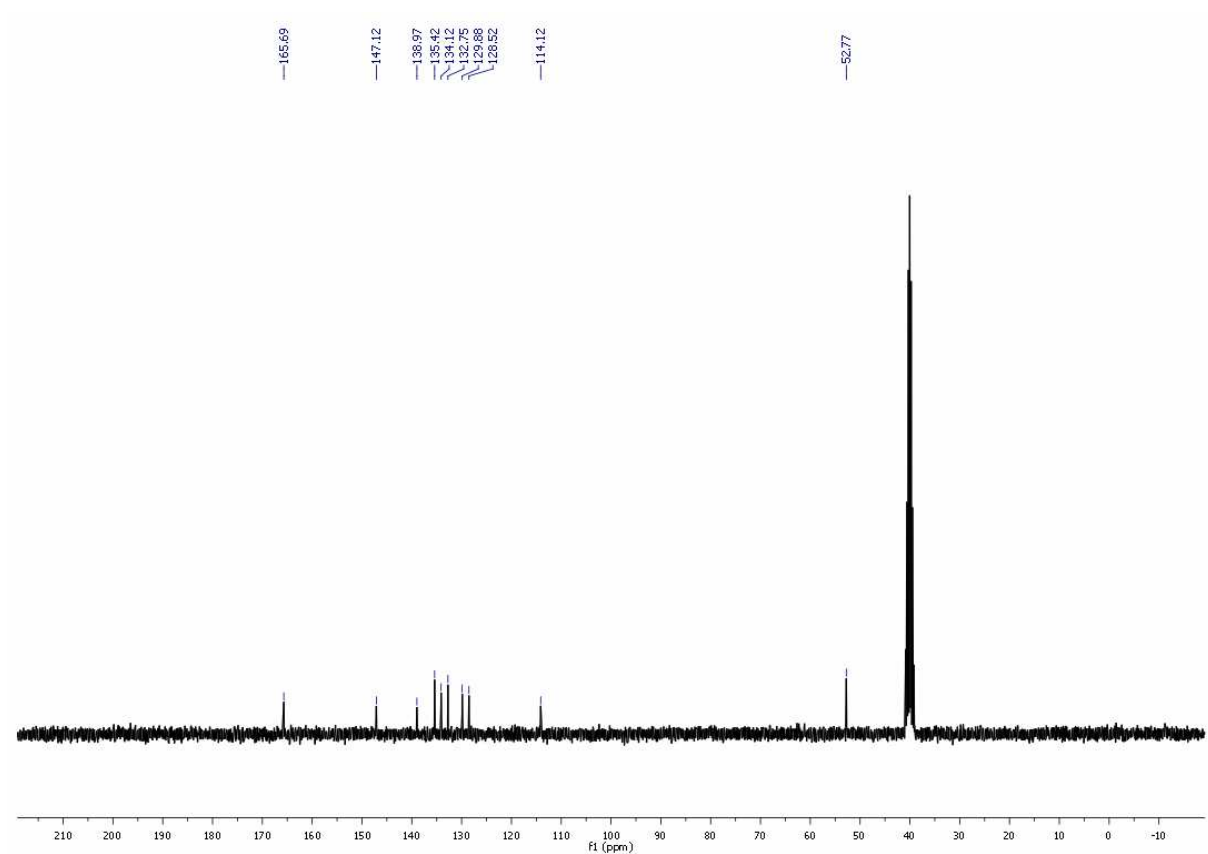
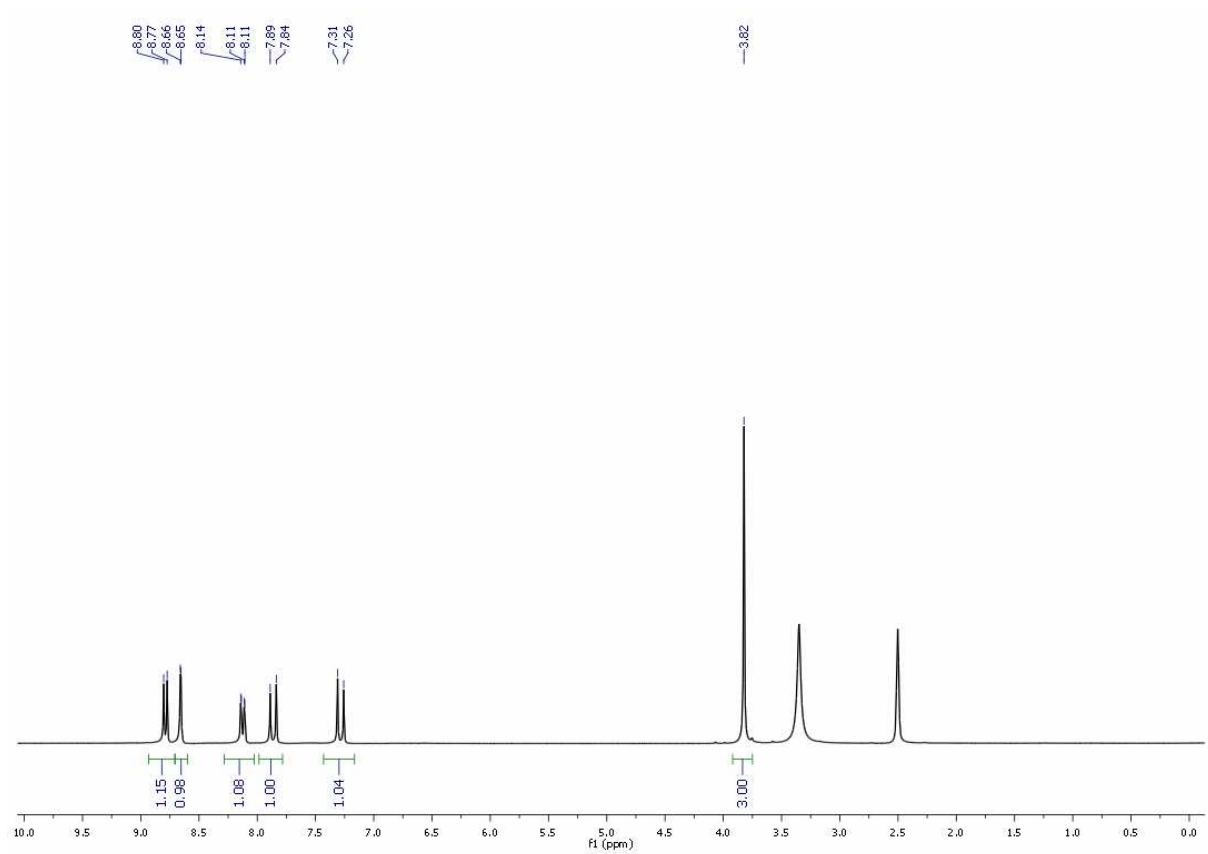


(*E*)-4-Chloro-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (**3f**)

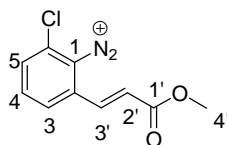


Following the general procedure, (*E*)-4-chloro-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (**3f**) was obtained from (*E*)-methyl 3-(2-acetamido-5-chlorophenyl)acrylate (**2f**) (0.5 mmol, 127 mg) as a beige-coloured solid (43 %, 0.2 mmol, 67 mg).

¹H NMR (300 MHz, DMSO) δ 8.79 (d, *J* = 8.9 Hz, 1H, 6-H), 8.66 (d, *J* = 1.8 Hz, 1H, 3-H), 8.12 (dd, *J* = 1.8, 8.9 Hz, 1H, 5-H), 7.86 (d, *J* = 15.7 Hz, 1H, 1'-H), 7.28 (d, *J* = 15.7 Hz, 1H, 2'-H), 3.82 (s, 3H, 4'-H). ¹³C NMR (75 MHz, DMSO) δ 165.7, 147.1, 138.9, 135.4, 134.1, 132.8, 129.9, 128.5, 114.1, 52.7. HRMS (EI) *m/z* calcd for C₁₀H₈N₂O₂Cl [M]⁺: 223.0274, found 223.0280. IR, ν 3420 (m), 2273 (s), 1717 (s), 1546 (s), 1297 (s).

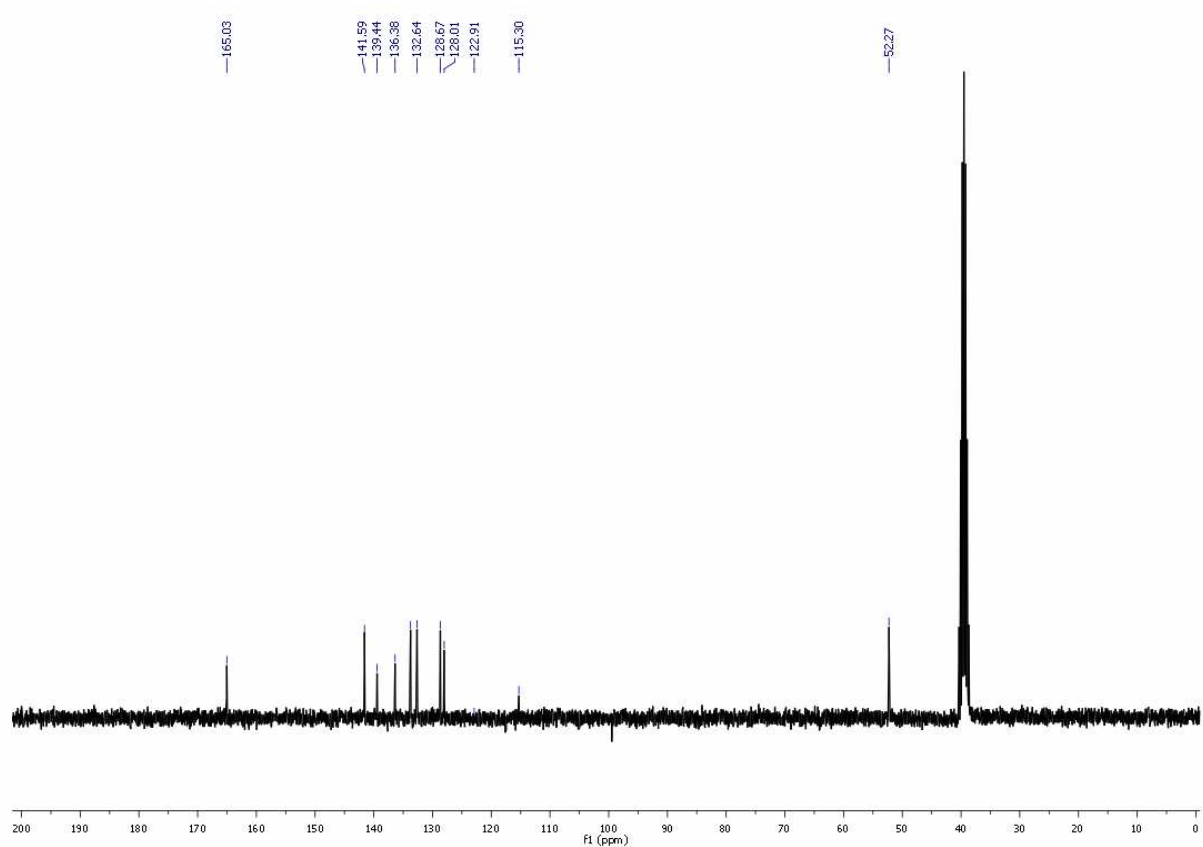
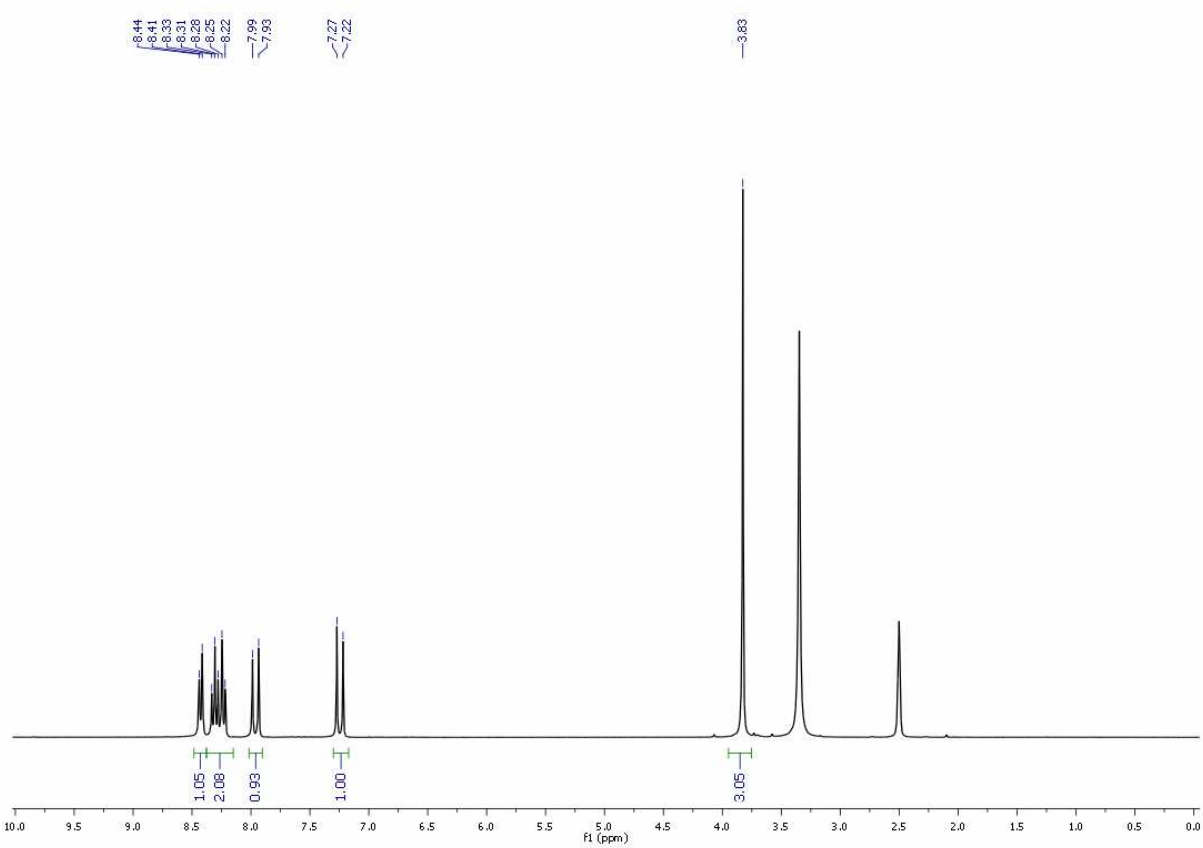


(*E*)-6-Chloro-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (**3g**)

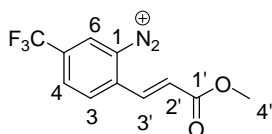


Following the general procedure, (*E*)-6-chloro-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (**3g**) was obtained from (*E*)-methyl 3-(2-acetamido-3-chlorophenyl)acrylate (**2g**) (2.0 mmol, 506 mg) as a beige-coloured solid (50 %, 1.01 mmol, 313 mg).

¹H NMR (300 MHz, DMSO) δ 8.43 (d, J = 7.5 Hz, 1H, 5-H), 8.31 (t, J = 8.1 Hz, 1H, 4-H), 8.23 (dd, J = 1.0, 8.1 Hz, 1H, 3-H), 7.96 (d, J = 15.7 Hz, 1H, 1'-H), 7.24 (d, J = 15.6 Hz, 1H, 2'-H), 3.83 (s, 3H, 4'-H). **¹³C NMR (75 MHz, DMSO)** δ 165.0, 141.6, 139.4, 136.4, 133.7, 132.6, 128.7, 128.0, 115.3, 52.3. **HRMS (EI)** m/z calcd for C₁₀H₈N₂O₂Cl [M]⁺: 223.0274, found 223.0295. **IR** ν 3162 (m), 2255 (m), 1708 (s), 1467 (s), 1217 (s).

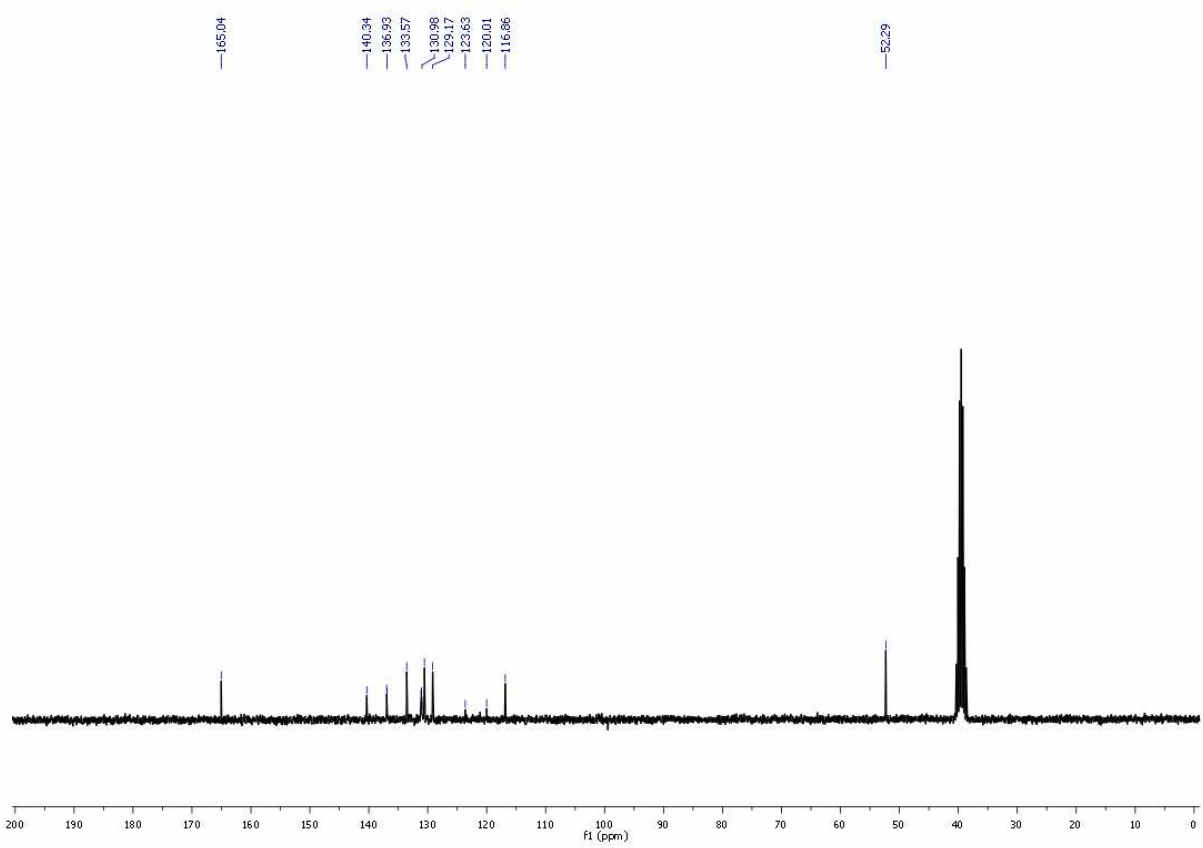
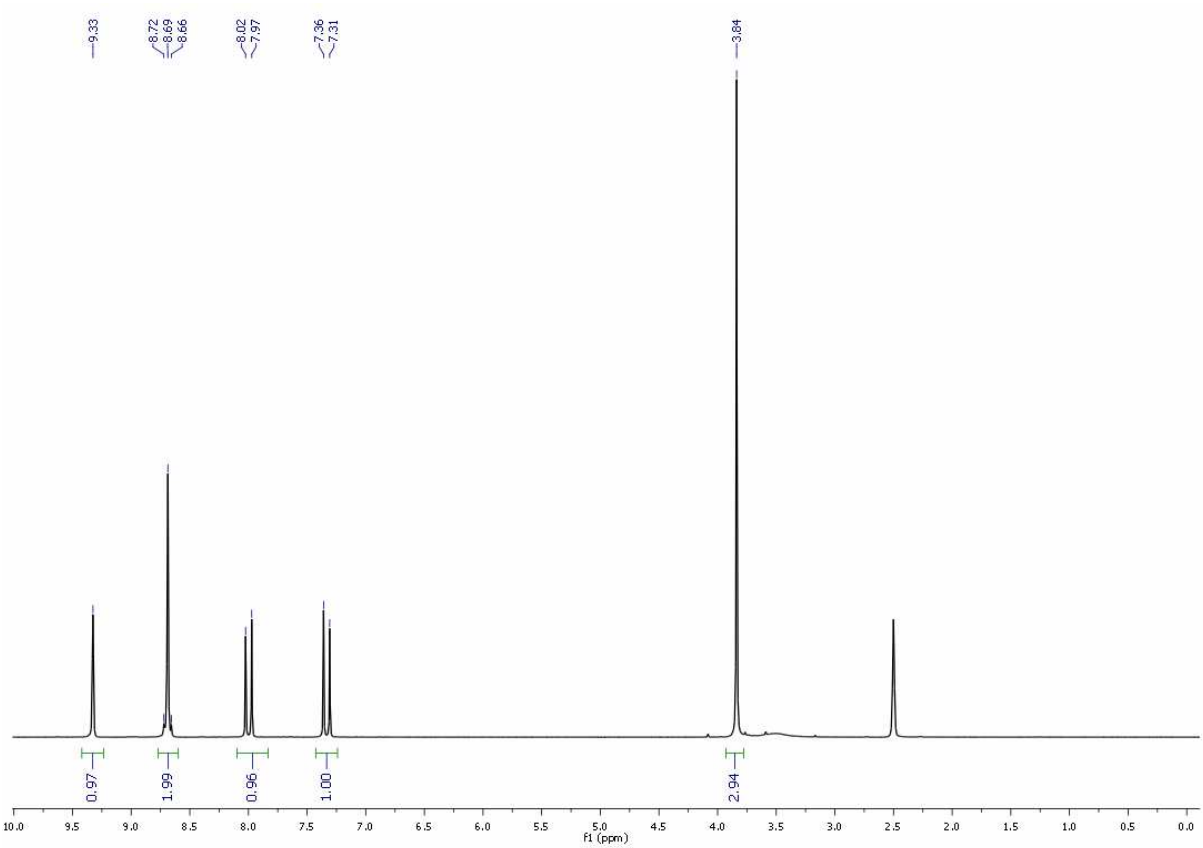


(*E*)-6-Trifluoromethyl-2-(3-Methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate
(**3h**)

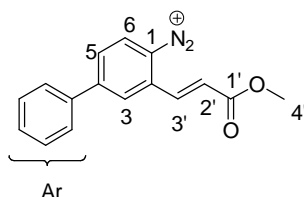


Following the general procedure, (*E*)-6-trifluoromethyl-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (**3h**) was obtained from (*E*)-methyl 3-(2-acetamido-4-(trifluoromethyl)-phenyl)acrylate (**2h**) (1.0 mmol, 287 mg) as a beige-coloured solid (77 %, 0.77 mmol, 265 mg).

¹H NMR (300 MHz, DMSO) δ 9.33 (s, 1H, 6-H), 8.69 (d, *J* = 9 Hz, 2H, 3/4-H), 8.68 (d, *J* = 9 Hz, 2H, 4/3-H), 8.00 (d, *J* = 15.7 Hz, 1H, 1'-H), 7.33 (d, *J* = 15.7 Hz, 1H, 2'-H), 3.84 (s, 3H, 4'-H). ¹³C NMR (75 MHz, DMSO) δ 165.0, 140.3, 136.9 (q, ³*J* = 3.0 Hz), 133.6, 131.1 (q, ³*J* = 4.5 Hz), 130.6, 129.2, 121.8 (q, ¹*J* = 271.5 Hz), 116.9, 52.8. HRMS (EI) *m/z* calcd for C₁₁H₈N₂O₂F₃ [M]⁺: 257.0538, found 257.0549. IR ν 3311 (w), 2260 (m), 1716 (s), 1556 (m), 1294 (s).

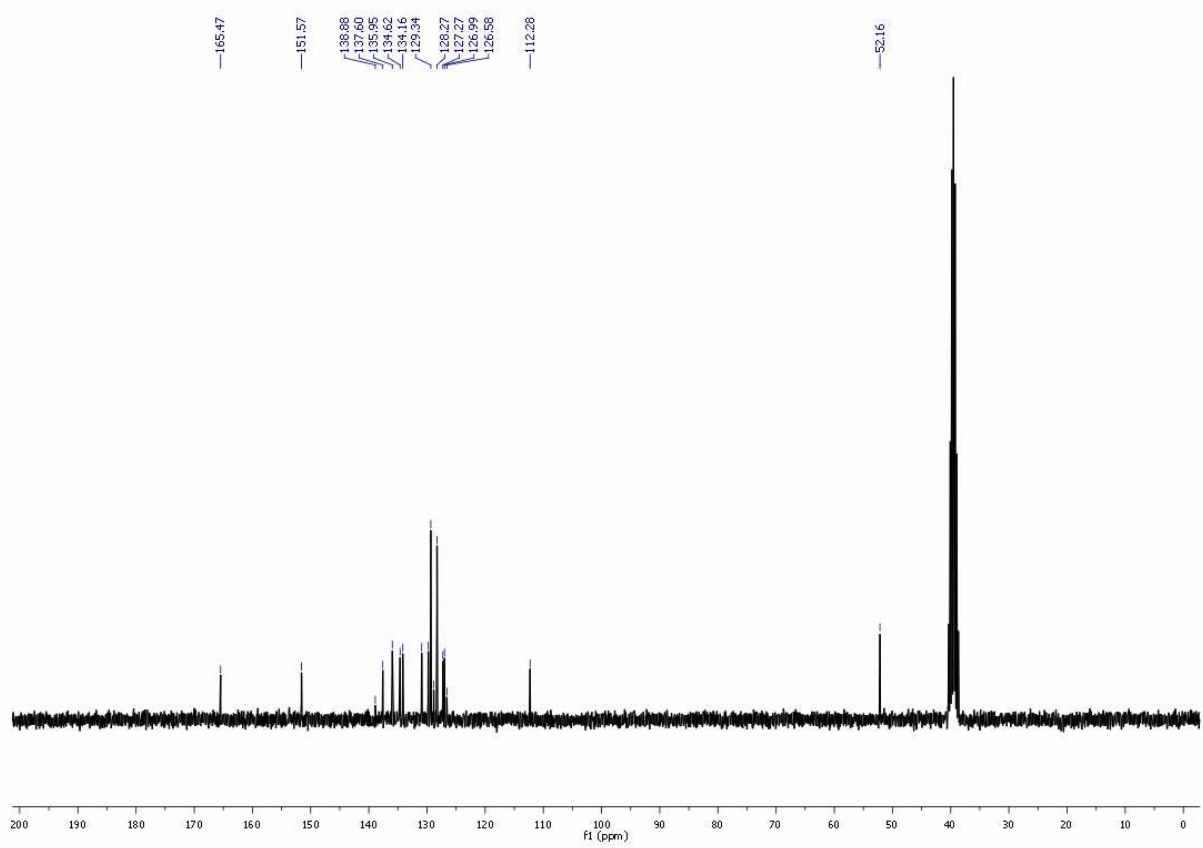
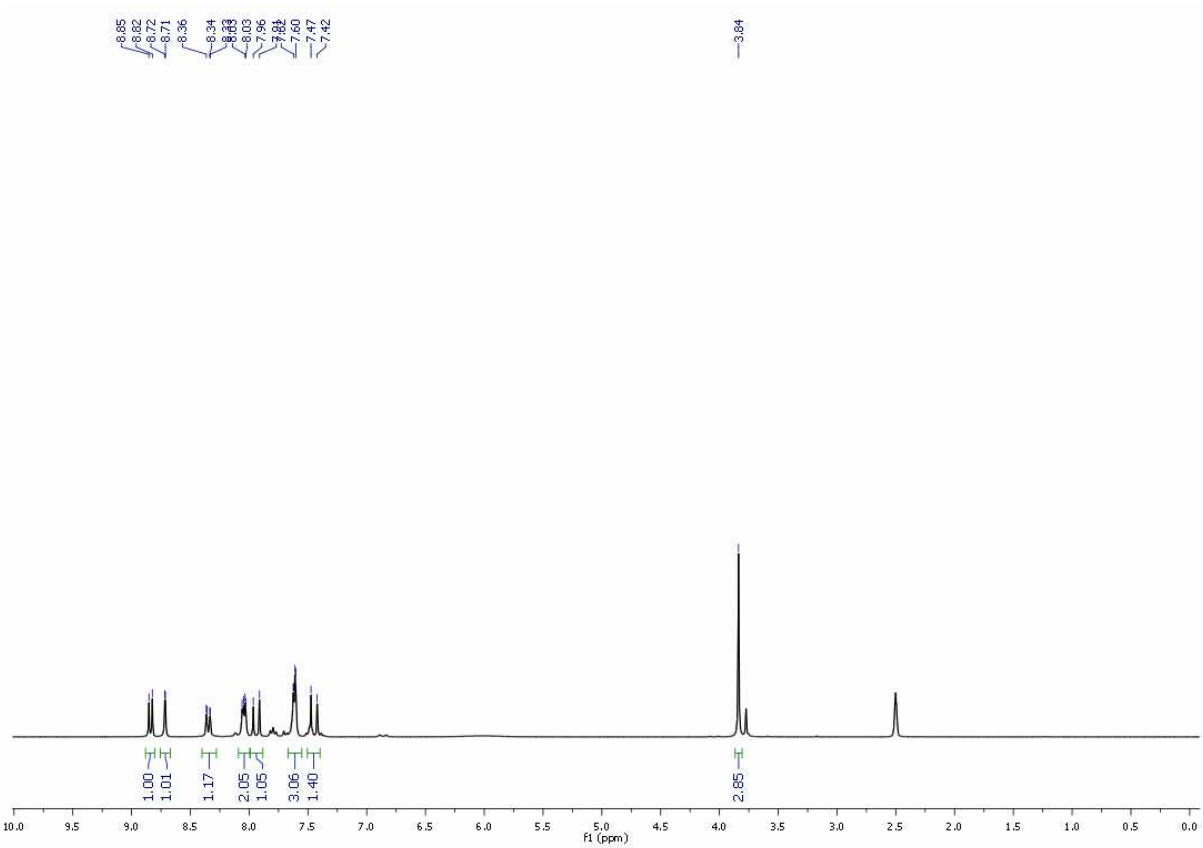


(*E*)-3-(3-Methoxy-3-oxoprop-1-enyl)biphenyl-4-diazonium tetrafluoroborate (**3i**)



Following the general procedure, (*E*)-3-(3-methoxy-3-oxoprop-1-enyl)biphenyl-4-diazonium tetrafluoroborate (**3i**) was obtained from (*E*)-methyl 3-(4-acetamidobiphenyl-3-yl)acrylate (**2i**) (1.0 mmol, 295 mg) with *tert*-Butylnitrit (2.0 mmol, 240 μ L) as a white solid (60 %, 0.60 mmol, 211 mg).

^1H NMR (300 MHz, DMSO) δ 8.84 (d, J = 8.8 Hz, 1H, 6-H), 8.71 (d, J = 1.4 Hz, 1H, 3-H), 8.35 (dd, J = 1.6, 8.8 Hz, 1H, 5-H), 8.04 (dd, J = 3.1, 6.5 Hz, 2H, Ar-H), 7.94 (d, J = 15.7 Hz, 1H, 3'-H), 7.62 (m, 3H, Ar-H), 7.45 (d, J = 15.7 Hz, 1H, 2'-H), 3.84 (s, 3H, 4'-H). ^{13}C NMR (75 MHz, DMSO) δ 165.5, 151.6, 138.9, 137.6, 135.9, 134.6, 134.2, 130.9, 129.8, 129.3, 128.8, 128.3, 127.3, 126.9, 126.6, 112.3, 52.2. HRMS (**EI**) m/z calcd for $\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_2$ $[\text{M}]^+$: 265.0977, found 265.0989. IR ν 3427 (w), 2258 (m), 1703 (s), 1287 (m), 1080 (s).



General procedure for the synthesis of compounds 4:

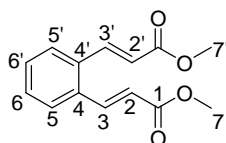
Synthesis via *Heck* reaction (method A)

To a solution of diazonium salt **3** (1.0 mmol) in anhydrous MeOH (3 mL) was added Pd(OAc)₂ (5 mol%, 11.2 mg). After 15 min methyl acrylate (1.2 mmol, 108 µL) was added. The solution was stirred for 12 h at room temperature. The reaction was quenched with water (15 mL) and extracted three times with ethyl acetate (60 mL). The combined organic layers were dried with Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography.

Synthesis via one flask sequence (method B)

To a solution of compound **2** (1.0 mmol) in dry methanol (6 mL) was added BF₃•MeOH (3.0 mmol, 324 µL). The solution was stirred 16 h at 70°C. The reaction was cooled to 0°C. *tert*-Butylnitrite (1.0 mmol, 120 µL) was added. After the diazonium salt precipitated, the reaction mixture was stirred 30 min., followed by addition of Pd(OAc)₂ (5 mol%, 11.2 mg). After 15 min methyl acrylate (1.2 mmol, 108 µL) was added. The solution was stirred for 12 h at room temperature. The reaction was quenched with water (15 mL) and extracted three times with ethyl acetate (60 mL). The combined organic layers were dried with Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography.

(2*E*, 2'*E*)-Dimethyl-3,3'-(1,2-phenylen)diacrylate (**4a**)

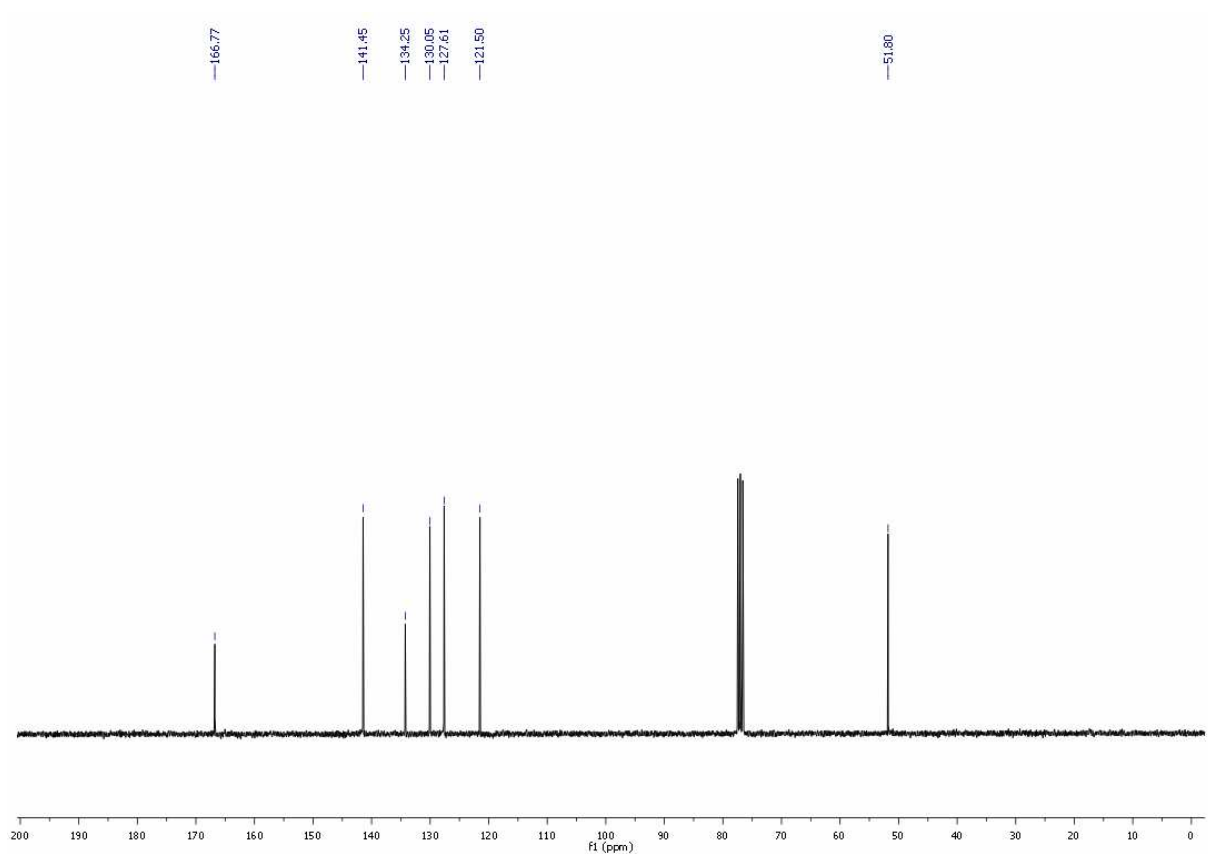
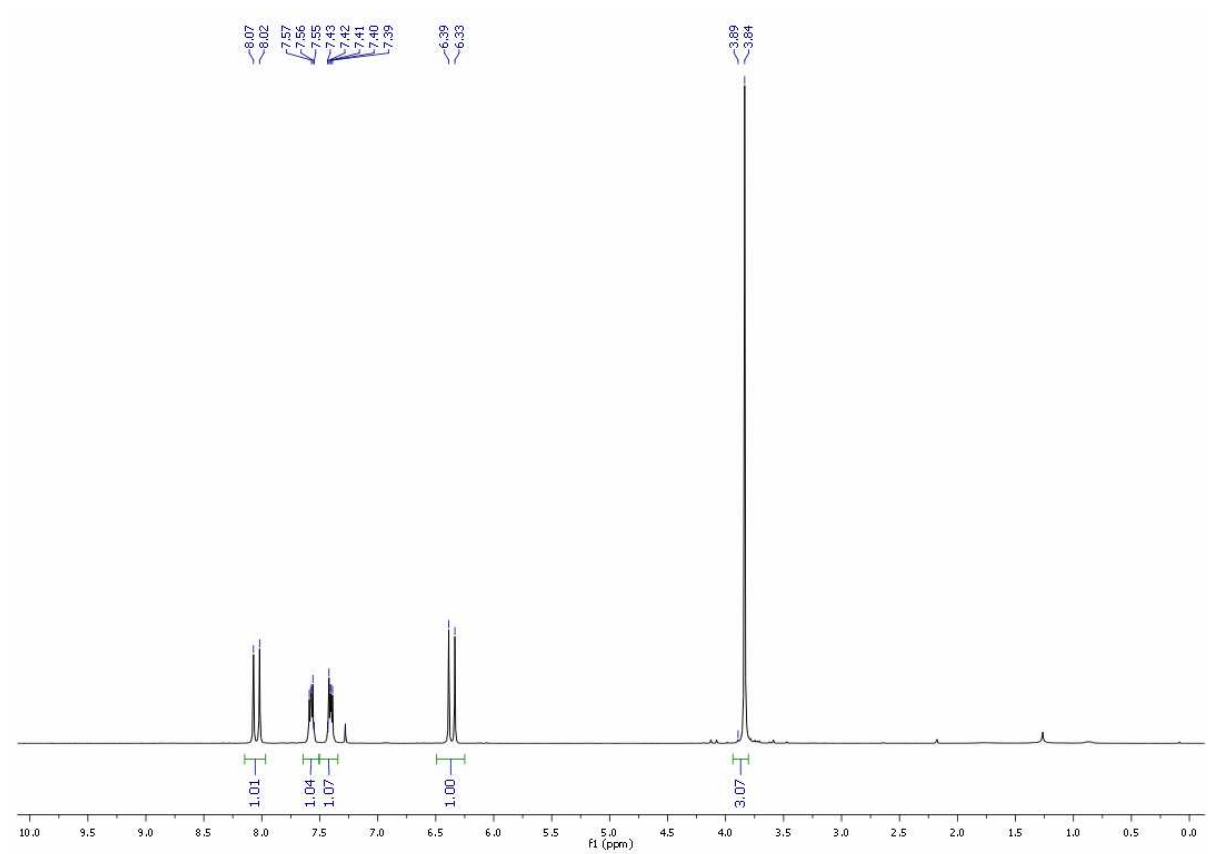


Following the general procedure (method A), **(2*E*,2'*E*)-dimethyl-3,3'-(1,2-phenylen)diacrylate (4a)** was obtained from (*E*)-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (**3a**) (0.18 mmol, 50 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 10:1) to afford **4a** as a colourless solid (90 %, 0.16 mmol, 40 mg).

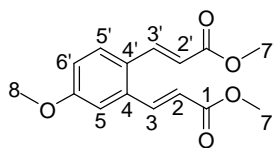
Following the general procedure (method B), **(2*E*,2'*E*)-dimethyl-3,3'-(1,2-phenylen)diacrylate (4a)** was obtained from (*E*)-methyl 3-(2-acetamidophenyl)acrylate (**2a**) (1.0 mmol, 219 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 10:1) to afford **4a** as a colourless solid (61 %, 0.61 mmol, 150 mg).

¹H NMR (300 MHz, CDCl₃) δ 7.96 (d, *J* = 15.8 Hz, 2H, 3-H, 3'-H), 7.79 (m, 2H, 5-H, 5'-H), 7.48 (m, 2H, 6-H, 6'-H), 6.55 (d, *J* = 15.8 Hz, 2H, 2-H, 2'-H), 3.76 (s, 6H, 7-H, 7'-H). **¹³C NMR (75 MHz, CDCl₃)** δ 166.8, 141.5, 134.3, 130.1, 127.6, 121.5, 51.8. **MS (EI)** *m/z* = 246 (3 %), 186 (59 %), 155 (76 %), 128 (100 %). **HRMS (EI)** *m/z* calcd for C₁₄H₁₄O₄ [M]⁺: 246.0887, found 246.0869. **IR** ν 2951 (w), 1712 (s), 1312 (s), 1168 (s), 975 (s). **mp** 70-72°C (Lit.:⁴ 68°C)

⁴ J. Fries, *Chem. Ber.*, 1936, **69**, 715.



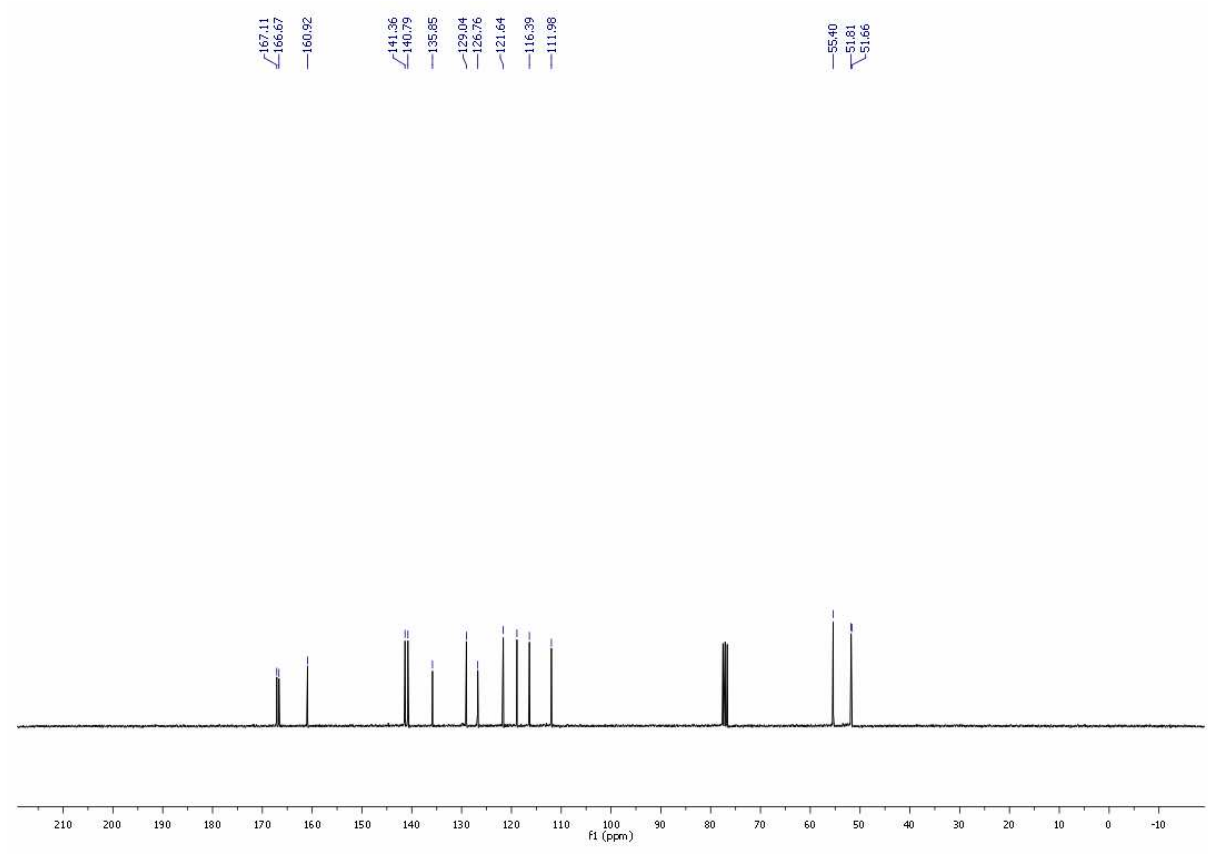
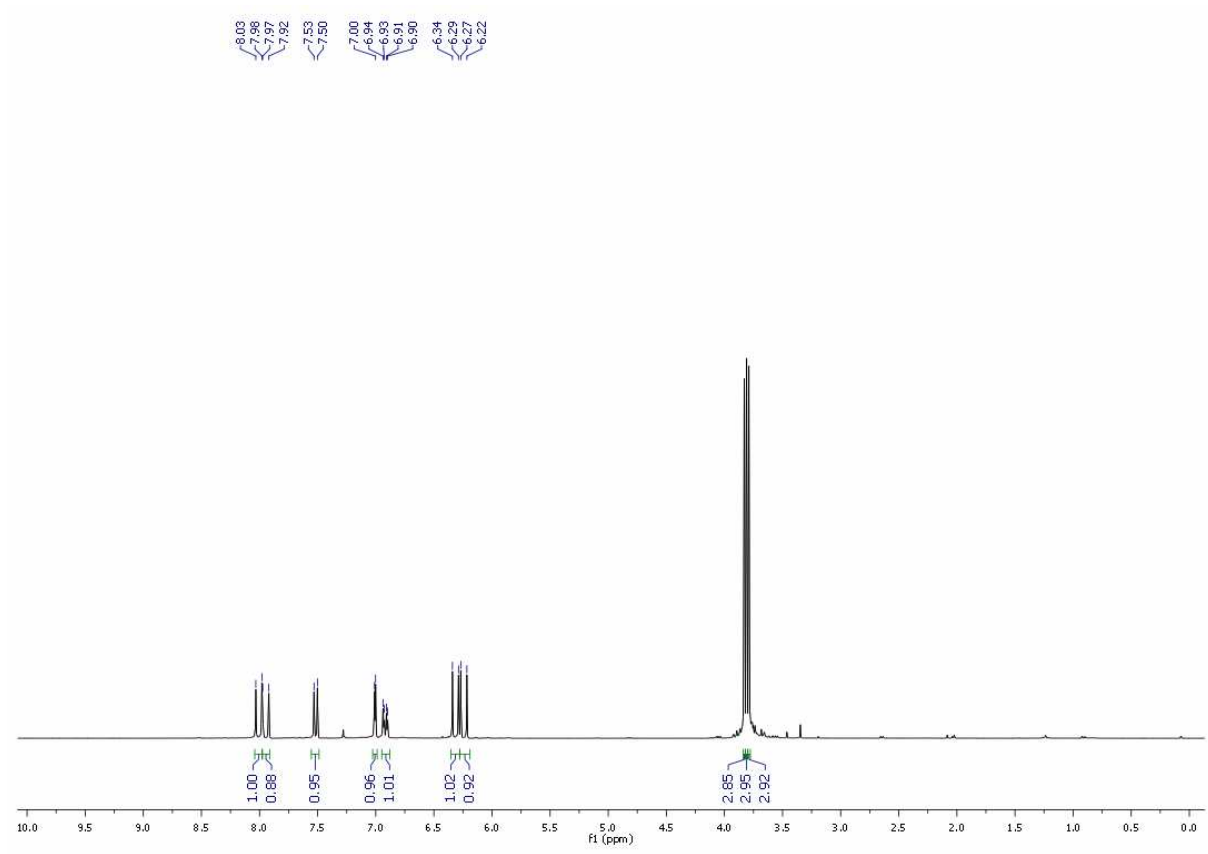
(2*E*, 2'*E*)-Dimethyl-3,3'-(4-methoxy-1,2-phenylen)diacrylate (**4b**)



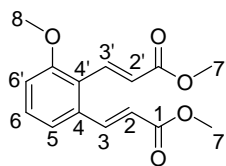
Following the general procedure (method A), **(2*E*,2'*E*)-dimethyl-3,3'-(4-methoxy-1,2-phenylen)diacrylate (4b)** was obtained from (*E*)-4-methoxy-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborat (**3b**) (0.5 mmol, 150 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 10:1) to afford **4b** as a colourless solid (>96 %, 0.49 mmol, 135 mg).

Following the general procedure (method B), **(2*E*,2'*E*)-dimethyl-3,3'-(4-methoxy-1,2-phenylen)diacrylate (4a)** was obtained from (*E*)-methyl 3-(2-acetamido-5-methoxyphenyl)acrylate (**2b**) (1.0 mmol, 249 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 10:1) to afford **4b** as a colourless solid (40 %, 0.39 mmol, 110 mg).

¹H NMR (300 MHz, CDCl₃) δ 7.95 (d, *J* = 15.8 Hz, 1H, 3'-H), 7.89 (d, *J* = 15.8 Hz, 1H, 3-H), 7.46 (d, *J* = 8.7 Hz, 1H, 5-H), 6.95 (d, *J* = 2.6 Hz, 1H, 5'-H), 6.86 (dd, *J* = 2.6, 8.7 Hz, 1H, 6'-H), 6.26 (d, *J* = 15.8 Hz, 1H, 2'-H), 6.19 (d, *J* = 15.8 Hz, 1H, 2-H), 3.77 (s, 3H, 8-H), 3.76 (s, 3H, 7'-H), 3.74 (s, 3H, 7-H). **¹³C NMR (75 MHz, CDCl₃)** δ 167.1, 166.6, 160.9, 141.3, 140.8, 135.8, 129.0, 126.7, 121.6, 118.9, 116.4, 111.9, 55.4, 51.8, 51.6. **MS (EI)** *m/z* = 276 (18 %), 216 (41 %), 158 (44 %), 115 (100 %). **HRMS (EI)** *m/z* calcd for C₁₅H₁₆O₅ [M]⁺: 276.0998, found 276.1008. **Anal.** calcd for C₁₅H₁₆O₅: C, 65.2 %; H, 5.8 %, found C, 65.2 %; H, 6.0 %. **IR** ν 2951 (w), 1709 (s), 1598 (s), 1623 (s), 1035 (s). **mp** 98-100°C.



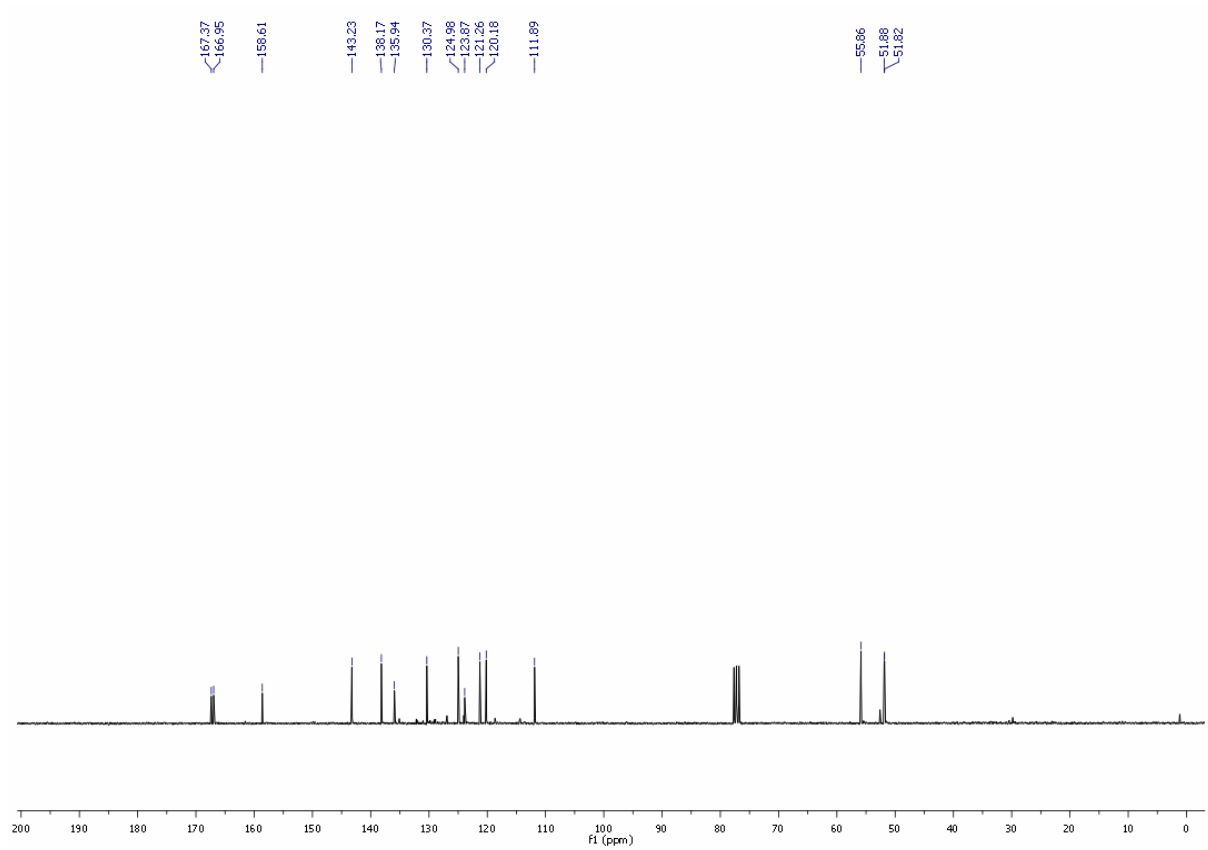
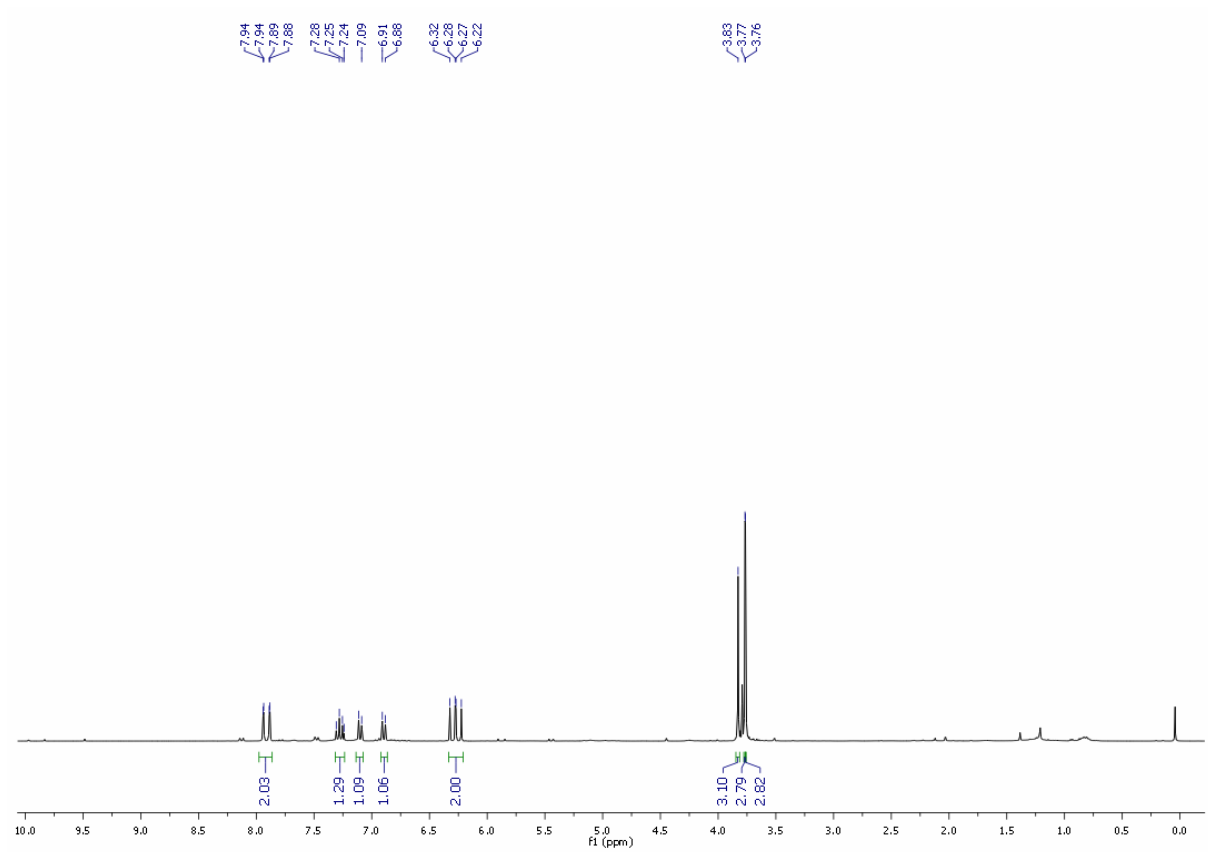
(2*E*, 2'*E*)-dimethyl-3,3'-(3-methoxy-1,2-phenylen)diacrylate (**4c**)



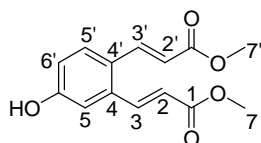
Following the general procedure (method A), **(2*E*,2'*E*)-dimethyl-3,3'-(3-methoxy-1,2-phenylen)diacrylate (4c)** was obtained from (*E*)-6-Methoxy-2-(3-Methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborat (**3c**) (1.0 mmol, 306 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 8:1) to afford **4c** as a colourless solid (>96 %, 0.98 mmol, 270 mg).

Following the general procedure (method B), **(2*E*,2'*E*)-dimethyl-3,3'-(3-methoxy-1,2-phenylen)diacrylate (4c)** was obtained from (*E*)-methyl 3-(2-acetamido-3-methoxyphenyl)acrylate (**2c**) (1.0 mmol, 249 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 8:1) to afford **4c** as a colourless solid (51 %, 0.51 mmol, 141 mg).

¹H NMR (300 MHz, CDCl₃) δ 7.91 (d, *J*= 16.0 Hz, 2H, 3/3'-H), 7.90 (d, *J*= 16.0 Hz, 2H, 3'/3-H), 7.27 (t, *J*= 8.0 Hz, 1H, 3-H), 7.10 (d, *J* = 7.8 Hz, 1H, 5'/6-H), 6.90 (d, *J* = 8.0 Hz, 1H, 6/5'-H), 6.33 (d, *J* = 16.0 Hz, 1H, 2'/2-H), 6.27 (d, *J* = 15.8 Hz, 1H, 2/2'-H), 3.83 (s, 3H, 8-H), 3.77 (s, 3H, 7'/7-H), 3.76 (s, 3H, 7/7'-H). **¹³C NMR (75 MHz, CDCl₃)** δ 167.2, 166.8, 158.5, 143.1, 138.0, 135.8, 130.2, 124.8, 123.7, 121.1, 120.0, 111.7, 55.7, 51.7, 51.7. **MS (EI)** *m/z* = 276 (18 %), 216 (100 %), 158 (78 %), 115 (45 %). **HRMS (EI)** *m/z* calcd for C₁₅H₁₆O₅ [M]⁺: 276.0998, found 276.0982. **Anal.** calcd for C₁₅H₁₆O₅: C, 65.2 %; H, 5.8 %, found C, 65.5 %; H, 6.2 %. **IR**, ν 2947 (w), 1713 (s), 1571 (m), 1169 (s), 1070 (s). **mp** 48-50°C.



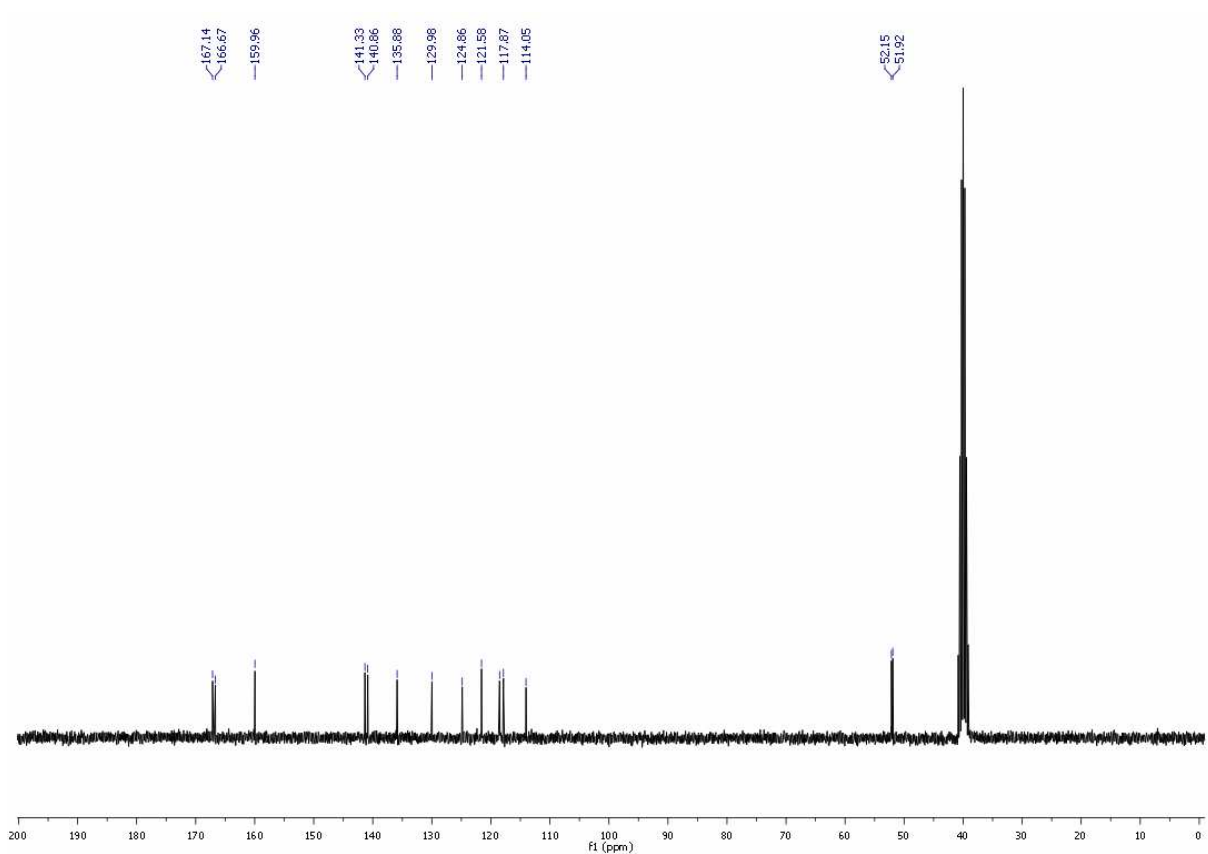
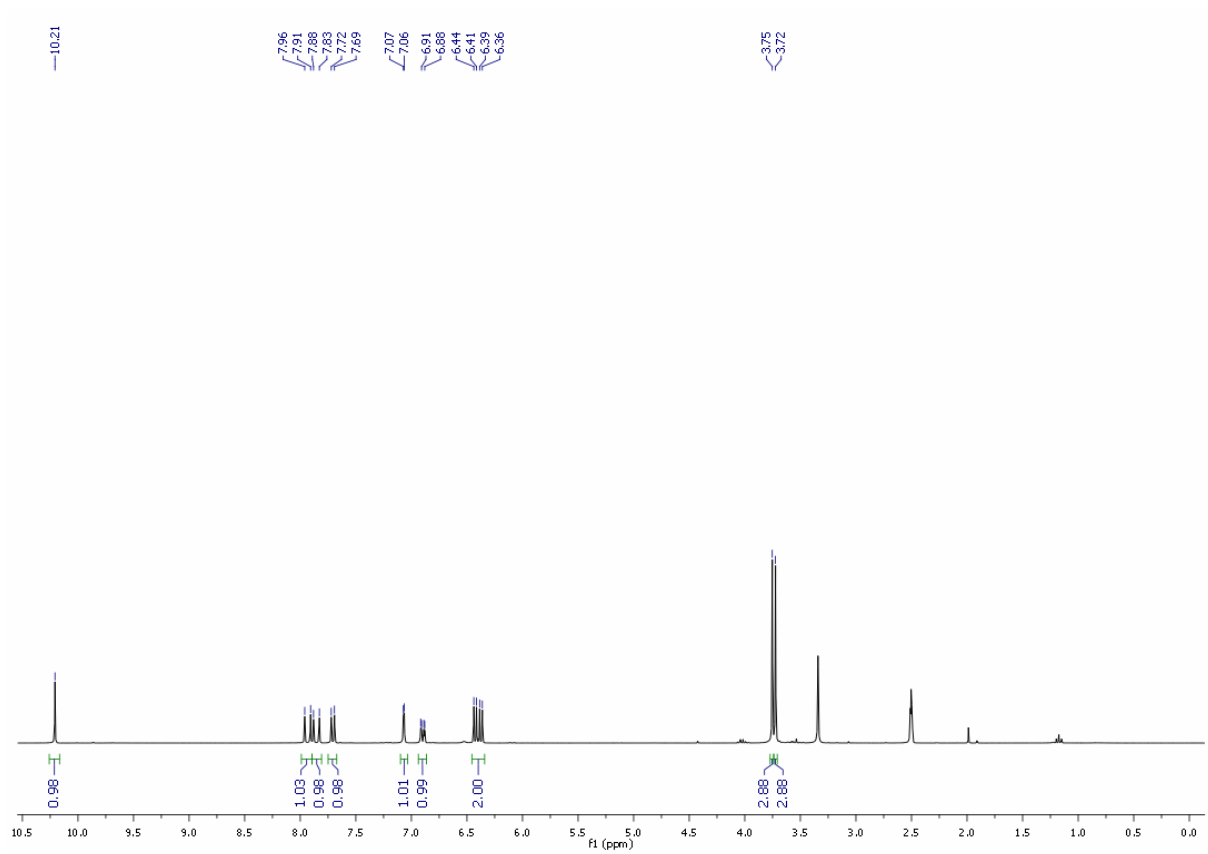
(2*E*, 2'*E*)-Dimethyl-3,3'-(4-hydroxy-1,2-phenylen)diacrylat (**4d**)



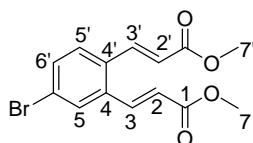
Following the general procedure (method A), **(2*E*,2'*E*)-dimethyl-3,3'-(4-hydroxy-1,2-phenylen)diacrylate (4d)** was obtained from (*E*)-4-hydroxy-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborat (**3d**) (1.0 mmol, 292 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 6:1) to afford **4d** as a colourless solid (>96 %, 0.99 mmol, 260 mg).

Following the general procedure (method B), **(2*E*,2'*E*)-dimethyl-3,3'-(4-hydroxy-1,2-phenylen)diacrylate (4d)** was obtained from (*E*)-methyl 3-(2-acetamido-5-hydroxyphenyl)acrylate (**2d**) (0.5 mmol, 118 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 6:1) to afford **4d** as a colourless solid (43 %, 0.21 mmol, 56 mg).

¹H NMR (300 MHz, CDCl₃) δ 10.21 (s, 1H, -OH), 7.93 (d, *J* = 15.8 Hz, 1H, 3'-H/3-H), 7.85 (d, *J* = 15.8 Hz, 1H, 3-H, 3'-H), 7.71 (d, *J* = 8.6 Hz, 1H, 5'-H), 7.07 (d, *J* = 2.5 Hz, 1H, 5-H), 6.90 (dd, *J* = 2.5, 8.6 Hz, 1H, 6'-H), 6.42 (d, *J* = 15.8 Hz, 1H, 2/2'-H), 6.39 (d, *J* = 15.7 Hz, 1H, 2/2'-H), 3.75 (s, 3H, 7'-H), 3.72 (s, 3H, 7-H). **¹³C NMR (75 MHz, CDCl₃)** δ 167.1, 166.7, 160.0, 141.3, 140.9, 135.9, 130.0, 124.9, 121.6, 118.5, 117.9, 114.1, 52.2, 51.9. **MS (EI)** *m/z* = 262 (6 %), 171 (34 %), 144 (100 %), 115 (72 %). **HRMS (EI)** *m/z* calcd for C₁₄H₁₄O₅ [M]⁺: 262.0836, found 262.0817. **IR** ν 3327 (w), 2952 (w), 1716 (m), 1236 (m), 1208 (s). **mp** 200-204°C.



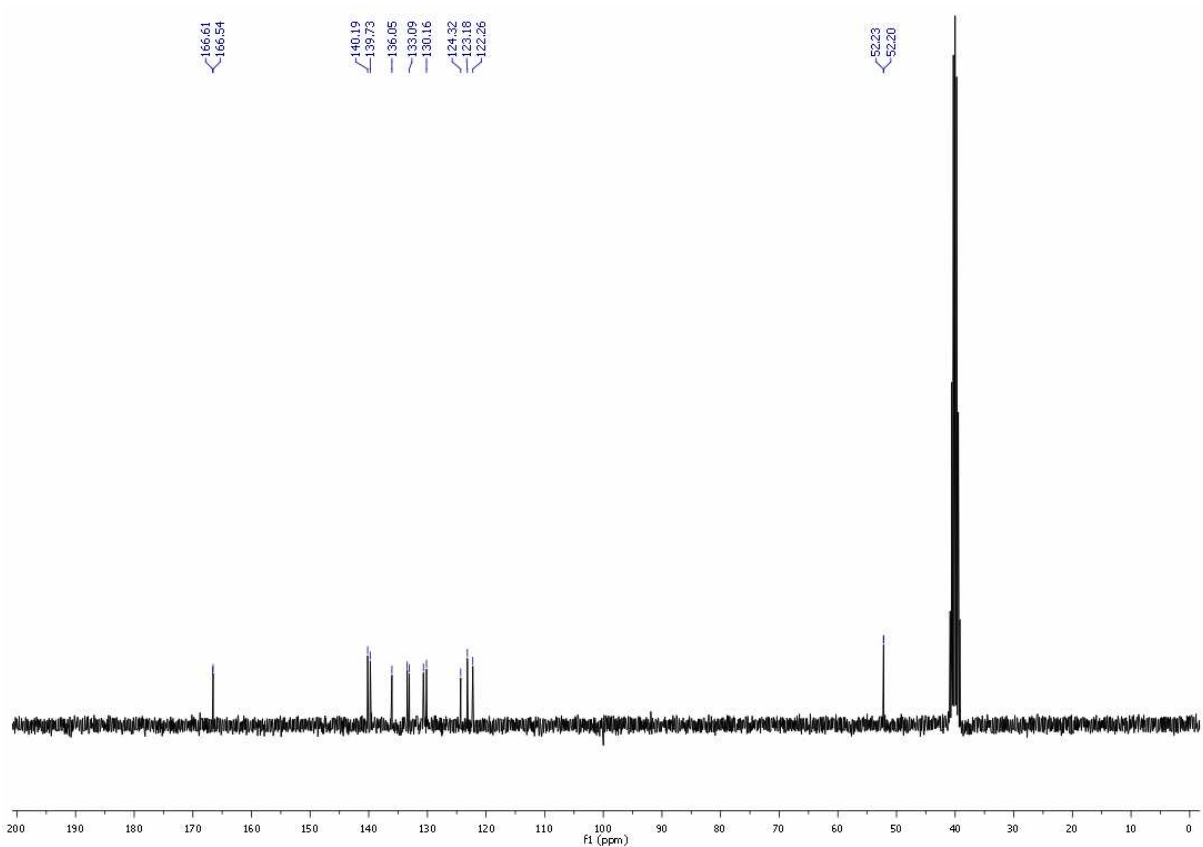
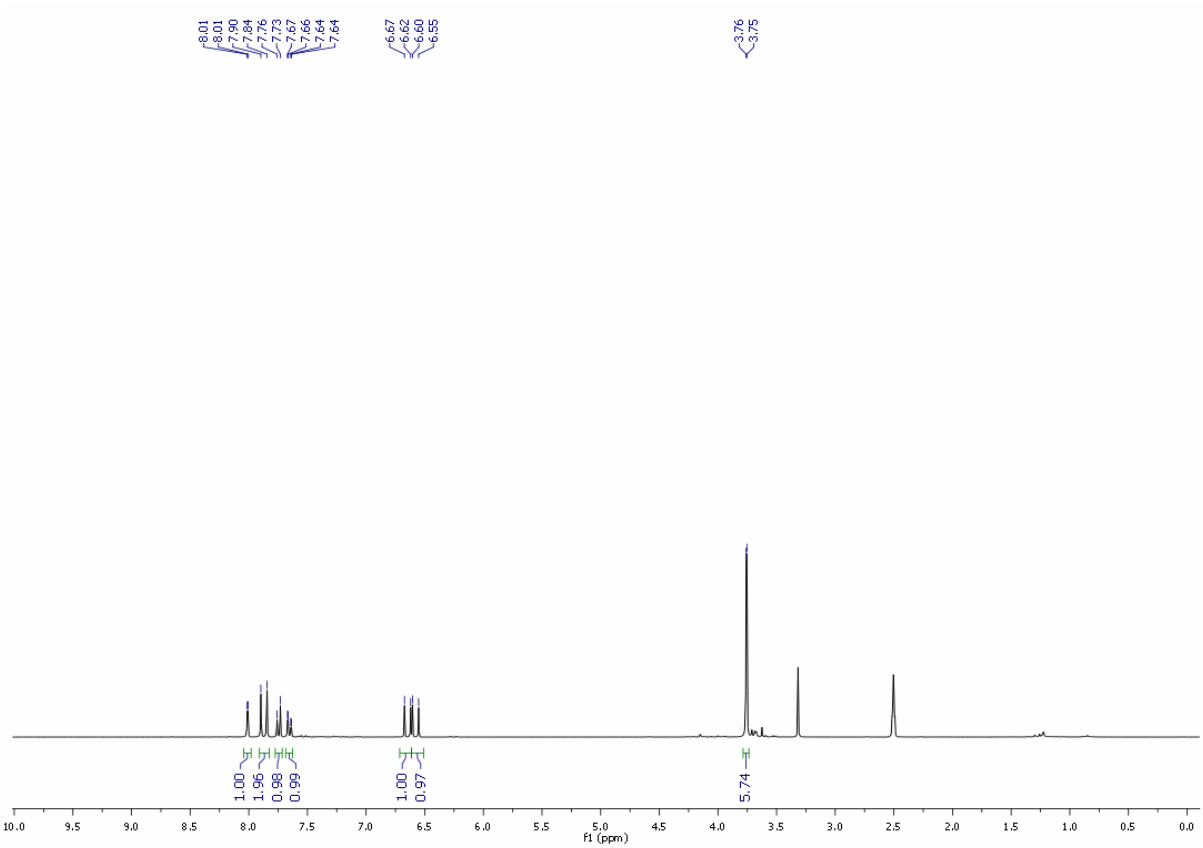
(2*E*, 2'*E*)-Dimethyl-3,3'-(4-bromo-1,2-phenylen)diacrylate (**4e**)



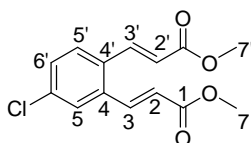
Following the general procedure (method A), **(2*E*,2'*E*)-dimethyl-3,3'-(4-bromo-1,2-phenylen)diacrylate (4e)** was obtained from (*E*)-4-bromo-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborat (**3e**) (1.0 mmol, 354 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 8:1) to afford **4e** as a colourless solid (>96 %, 0.99 mmol, 322 mg).

Following the general procedure (method B), **(2*E*,2'*E*)-dimethyl-3,3'-(4-bromo-1,2-phenylen)diacrylate (4e)** was obtained from (*E*)-Methyl 3-(2-acetamido-5-bromophenyl)acrylate (**2e**) (0.5 mmol, 149 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 8:1) to afford **4e** as a colourless solid (49 %, 0.25 mmol, 80 mg).

¹H NMR (300 MHz, CDCl₃) δ 7.93 (d, *J* = 15.8 Hz, 1H, 3'/3-H), 7.91 (d, *J* = 15.8 Hz, 1H, 3/3'-H), 7.67 (d, *J* = 1.8 Hz, 1H, 5-H), 7.49 (dd, *J* = 1.8, 8.4 Hz, 1H, 6'-H), 7.40 (d, *J* = 8.4 Hz, 1H, 5'-H), 6.32 (d, *J* = 15.8 Hz, 1H, 2/2'-H), 6.31 (d, *J* = 15.8 Hz, 1H, 2'/2-H), 3.79 (s, 6H, 7-H, 7'-H). **¹³C NMR (75 MHz, CDCl₃)** δ 161.8, 161.6, 135.5, 135.2, 131.2, 128.3, 128.2, 125.7, 124.3, 119.6, 117.9, 117.2, 47.2, 47.1. **MS (EI)** *m/z* = 324 (10 %), 264 (70 %), 206 (28 %), 142 (100 %). **HRMS (EI)** *m/z* calcd for C₁₄H₁₃O₄Br [M]⁺: 323.9997, found 323.9974. **Anal.** calcd for C₁₄H₁₃O₄Br: C, 51.7 %; H, 4.0 %, found C, 51.4 %; H, 4.4 %. **IR** ν 2954 (w), 1716 (s), 1435 (m), 1319 (m), 1034 (m). **mp** 79-80°C.



(2*E*, 2'*E*)-Dimethyl-3,3'-(4-chloro-1,2-phenylen)diacrylate (**4f**)⁵

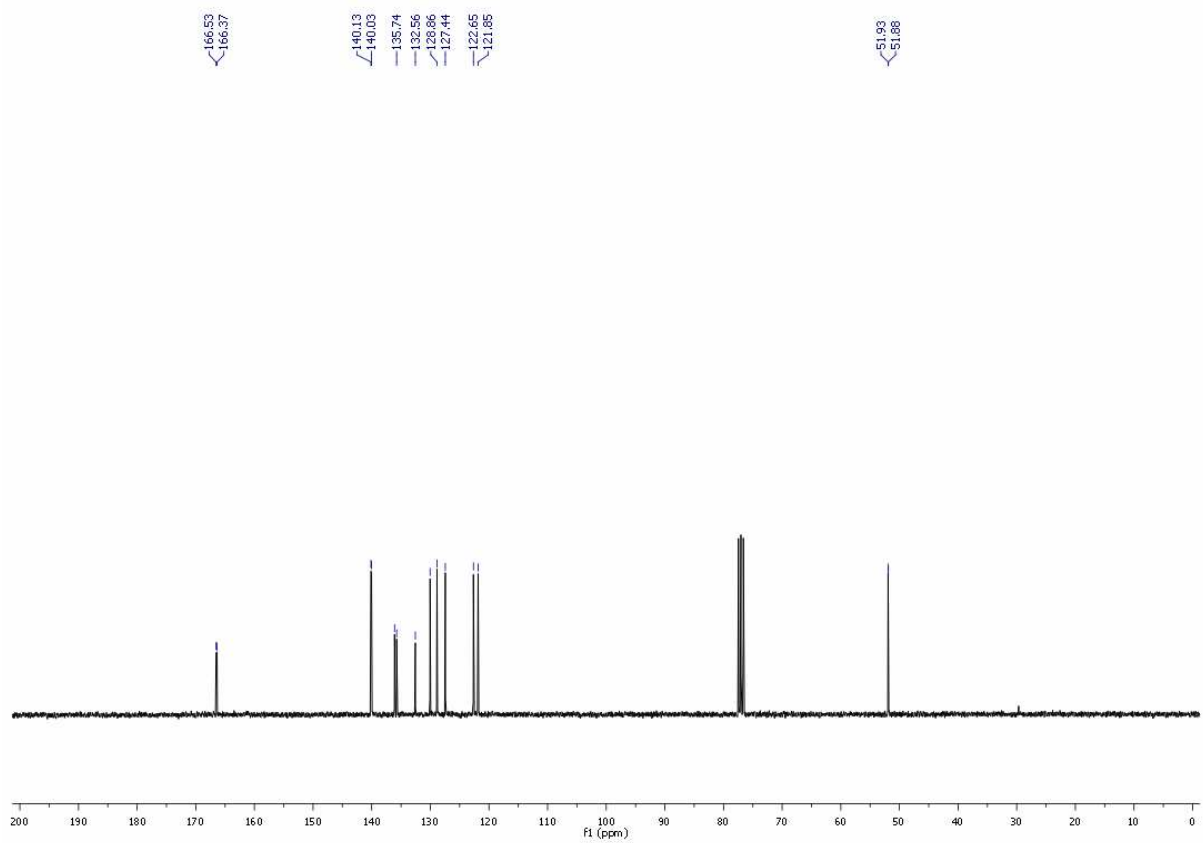
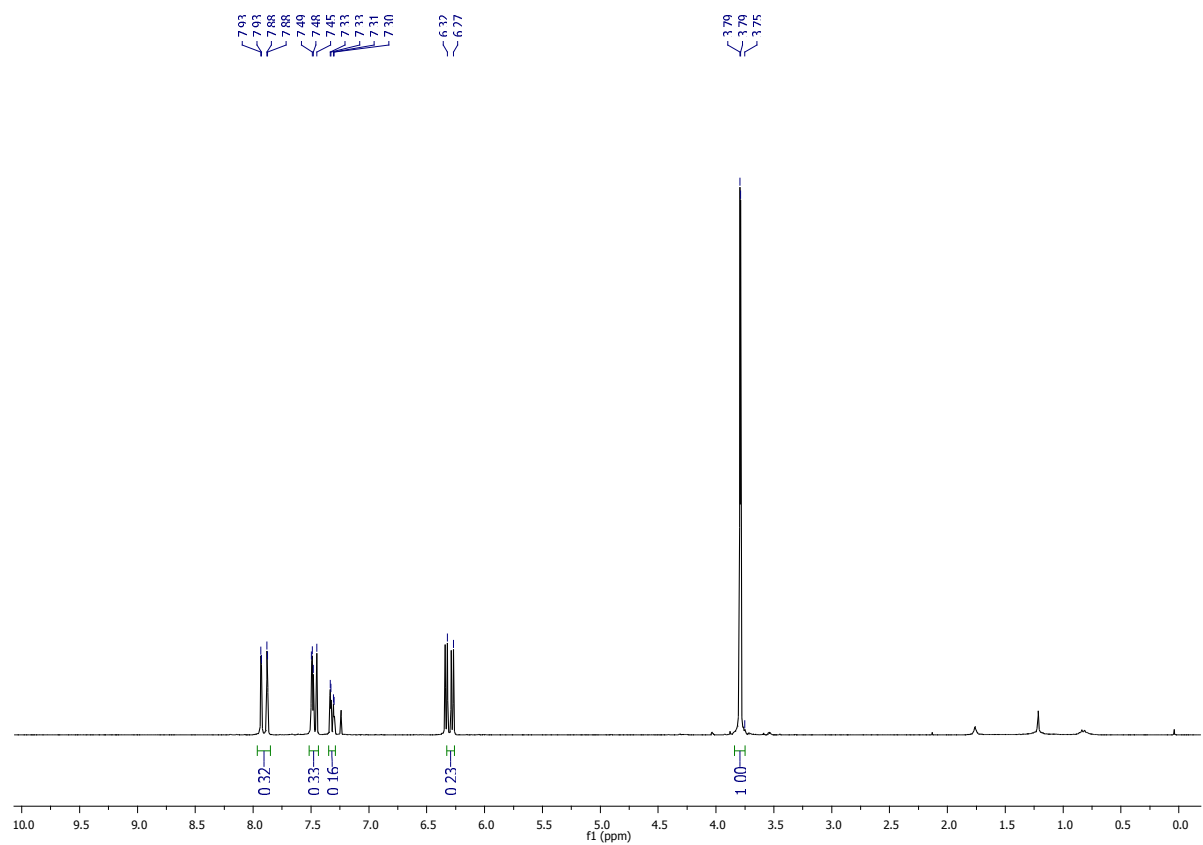


Following the general procedure (method A), **(2*E*,2'*E*)-dimethyl-3,3'-(4-chloro-1,2-phenylen)diacrylate (4f)** was obtained from (*E*)-4-chloro-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborat (**3f**) (0.32 mmol, 100 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 8:1) to afford **4f** as a colourless solid (76 %, 0.24 mmol, 68 mg).

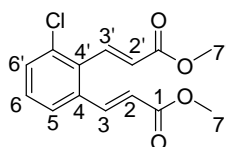
Following the general procedure (method B), **(2*E*,2'*E*)-dimethyl-3,3'-(4-chloro-1,2-phenylen)diacrylate (4f)** was obtained from (*E*)-Methyl 3-(2-acetamido-5-chlorophenyl)acrylate (**2f**) (0.36 mmol, 60 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 8:1) to afford **4f** as a colourless solid (49 %, 0.18 mmol, 49 mg).

¹H NMR (300 MHz, CDCl₃) δ 7.91 (d, *J* = 15.8 Hz, 1H, 3'-H/3-H), 7.89 (d, *J* = 15.8 Hz, 1H, 3-H, 3'-H), 7.49 (d, *J* = 2.1 Hz, 1H, 5-H), 7.47 (d, *J* = 8.5, 1H, 5'-H), 7.32 (dd, *J* = 2.1, 8.4 Hz, 1H, 6'-H), 6.31 (d, *J* = 15.8 Hz, 1H, 2'/2-H), 6.29 (d, *J* = 15.8 Hz, 1H, 2/2'-H), 3.80 (s, 3H, 7'/7-H), 3.79 (s, 3H, 7/7'-H). **¹³C NMR (75 MHz, CDCl₃)** δ 166.5, 166.4, 140.1, 140.0, 136.1, 135.7, 132.6, 130.0, 128.9, 127.4, 122.7, 121.8, 51.9, 51.9. **MS (EI)** *m/z* = 280 (10 %), 220 (100 %), 189 (75 %), 142 (55 %), 127 (48 %). **HRMS (EI)** *m/z* calcd for C₁₄H₁₃ClO₄ [M]⁺: 280.0502, found 280.0506. **Anal.** calcd for C₁₄H₁₃ClO₄: C, 59.9 %; H, 4.7 %, found C, 59.6 %; H, 4.4 %. **IR** ν 2955 (w), 1715 (m), 1432 (m), 1284 (m), 1168 (s). **mp** 97-102°C.

⁵ Ch. Wang, L.-Sh. Tan, J.-P. He, H.-W. Hu and J.-H. Xu, *Synth. Commun.*, 2003, **33**, 773.



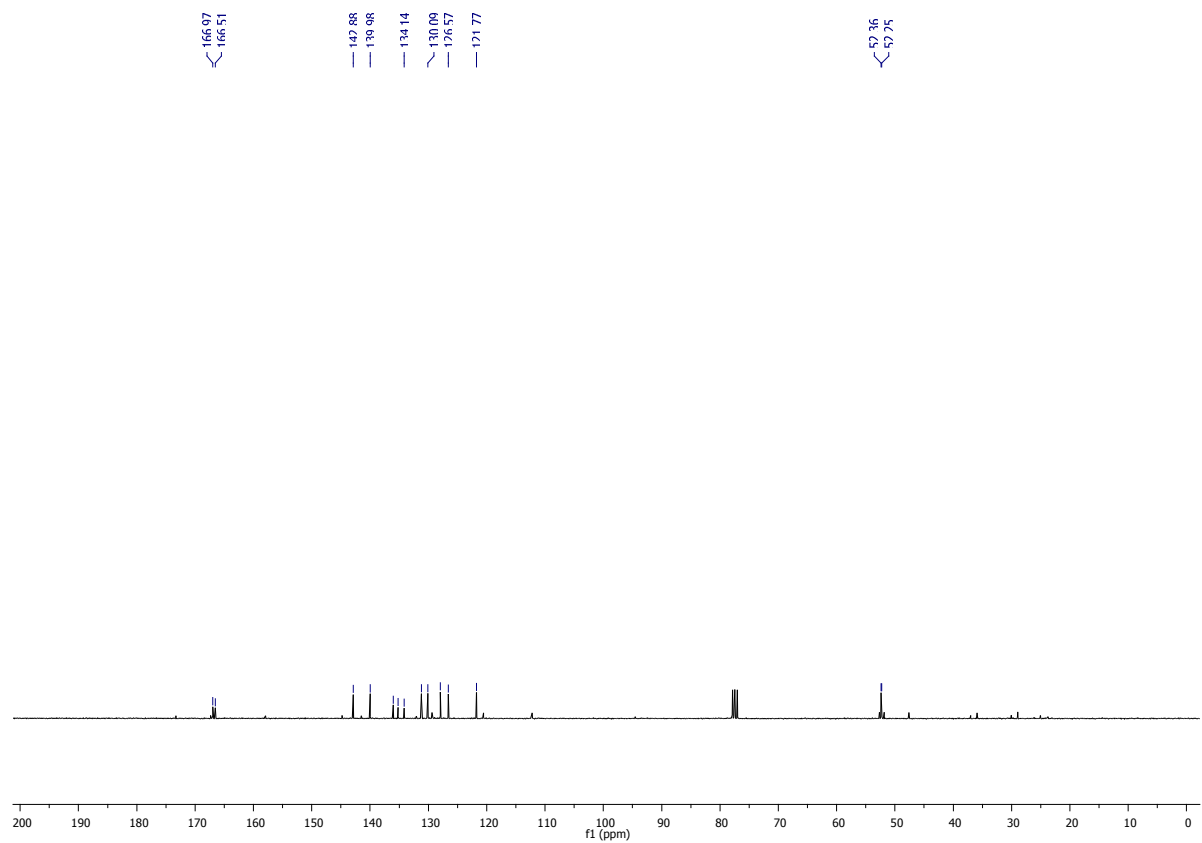
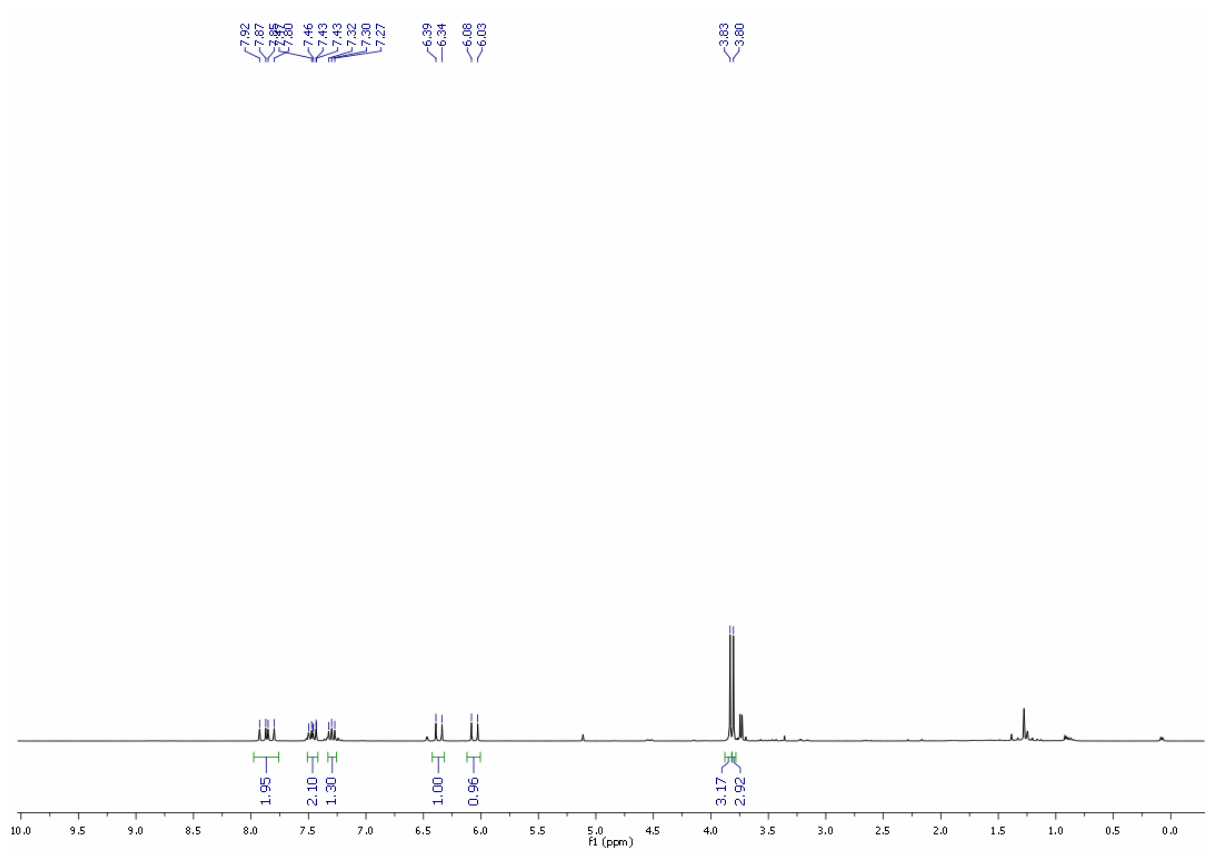
(2*E*, 2'*E*)-Dimethyl-3,3'-(3-chloro-1,2-phenylen)diacrylate (**4g**)



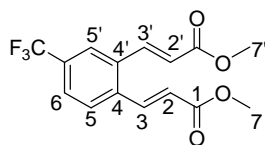
Following the general procedure (method A), **(2*E*,2'*E*)-dimethyl-3,3'-(3-chloro-1,2-phenylen)diacrylate (4g)** was obtained from (*E*)-6-chloro-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborat (**3g**) (0.26 mmol, 80 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 8:1) to afford **4g** as a colourless solid (37 %, 0.096 mmol, 27 mg).

Following the general procedure (method B), **(2*E*,2'*E*)-dimethyl-3,3'-(3-chloro-1,2-phenylen)diacrylate (4g)** was obtained from (*E*)-methyl 3-(2-acetamido-3-chlorophenyl)acrylate (**2g**) (1.0 mmol, 253 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 8:1) to afford **4g** as a colourless solid (14 %, 0.14 mmol, 39 mg).

¹H NMR (300 MHz, CDCl₃) δ 7.85 (d, *J* = 16.2 Hz, 1H, 3'-H/3-H), 7.83 (d, *J* = 15.9 Hz, 1H, 3-H/3'-H), 7.49 (d, *J* = 2.1 Hz, 1H, 5-H), 7.45 (dd, *J* = 7.7, 1H, 6'-H), 7.30 (t, *J* = 7.9 Hz, 1H, 5-H), 6.36 (d, *J* = 15.9 Hz, 1H, 2'/2-H), 6.06 (d, *J* = 16.2 Hz, 1H, 2/2'-H), 3.83 (s, 3H, 7'/7-H), 3.80 (s, 3H, 7/7'-H). **¹³C NMR (75 MHz, CDCl₃)** δ 166.9, 166.5, 142.9, 139.9, 136.1, 135.2, 134.1, 131.2, 130.1, 127.9, 126.6, 121.8, 52.4, 52.3. **MS (EI)** *m/z* = 280 (25 %), 220 (100 %), 189 (83 %), 142 (58 %), 127 (58 %). **HRMS (EI)** *m/z* calcd for C₁₄H₁₃ClO₄ [M]⁺: 280.0502, found 280.0493. **Anal.** calcd for C₁₄H₁₃ClO₄: C, 59.9 %; H, 4.7 %, found C, 59.8 %; H, 4.4 %. **IR** ν 2954 (w), 1720 (m), 1435 (w), 1283 (m), 1173 (s). **mp** 101-103°C.



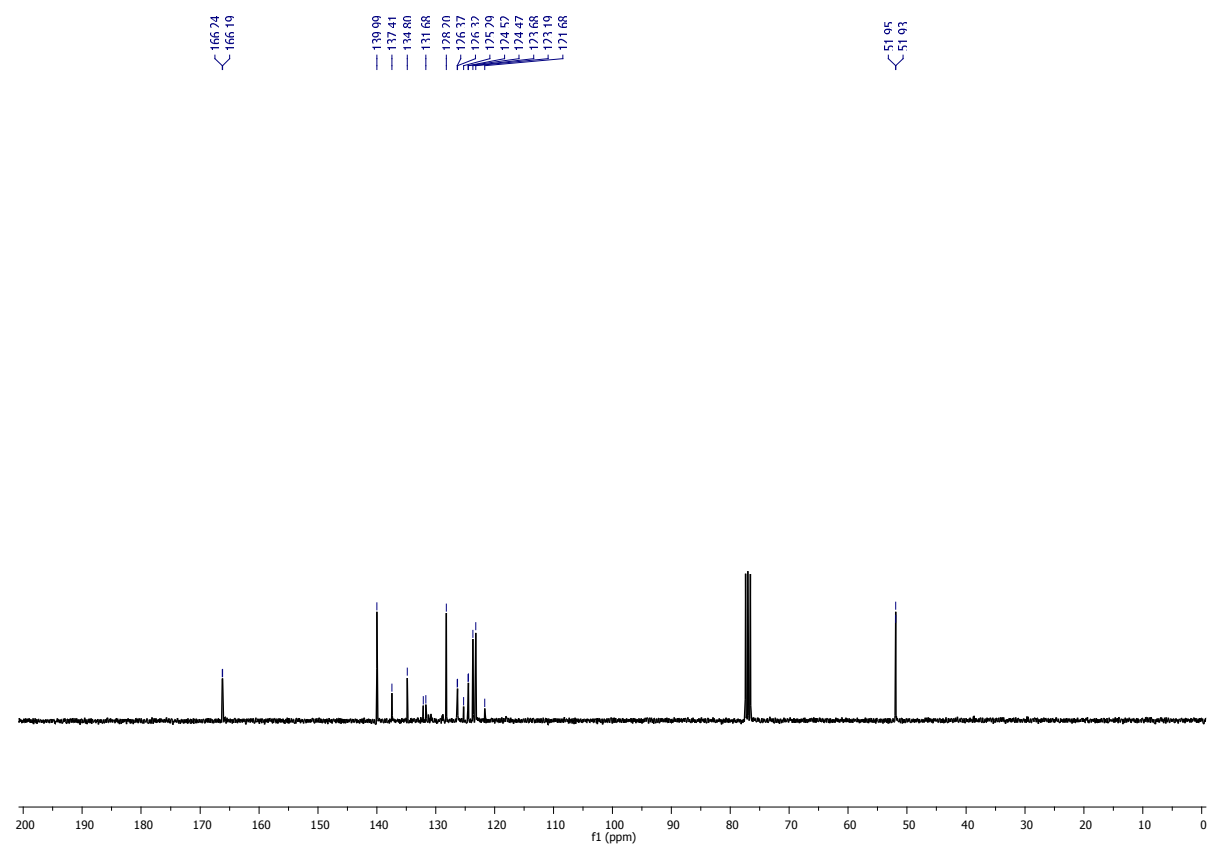
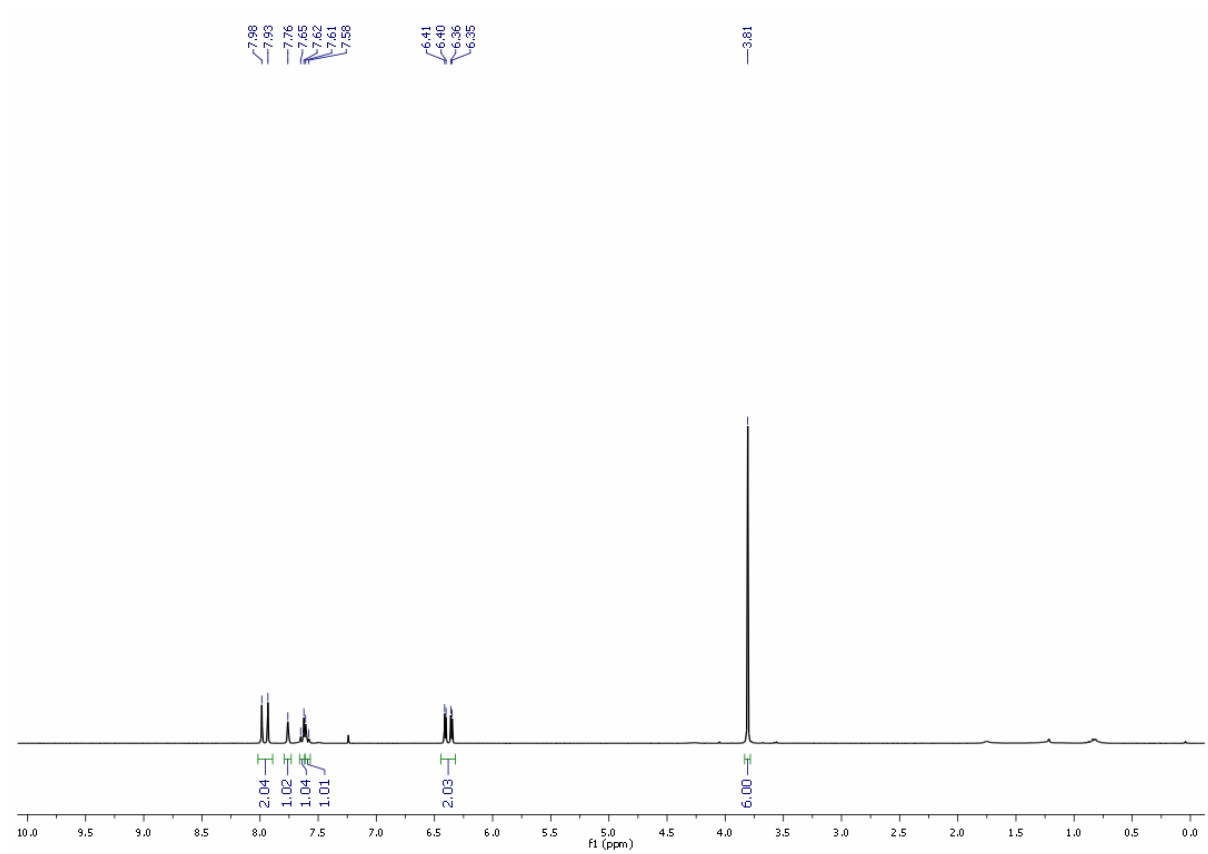
(2*E*, 2'*E*)-dimethyl-3,3'-(4-trifluoromethyl-1,2-phenylen)diacrylate (**4h**)



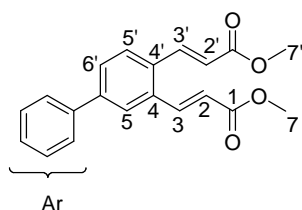
Following the general procedure (method A), (**2*E*,2'*E***)-dimethyl-3,3'-(4-trifluoromethyl-1,2-phenylen)diacrylate (**4h**) was obtained from (*E*)-6-Trifluoromethyl-2-(3-Methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborat (**3h**) (0.3 mmol, 100 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 8:1) to afford **4h** as a colourless solid (>96 %, 0.29 mmol, 92 mg).

Following the general procedure (method B), (**2*E*,2'*E***)-dimethyl-3,3'-(4-trifluoromethyl-1,2-phenylen)diacrylate (**4h**) was obtained from (*E*)-methyl 3-(2-acetamido-4-(trifluoromethyl)phenyl)acrylate (**2h**) (0.73 mmol, 210 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 8:1) to afford **4h** as a colourless solid (56 %, 0.41 mmol, 129 mg).

¹H NMR (300 MHz, CDCl₃) δ 7.96 (d, *J* = 15.9 Hz, 2H, 3'-H,3-H), 7.76 (s, 1H, 5'-H), 7.64 (d, *J* = 8.3 Hz, 1H, 5-H), 7.59 (d, *J* = 1.2, 8.4 Hz, 1H, 6-H), 6.38 (d, *J* = 15.9 Hz, 1H, 2'/2-H), 6.36 (d, *J* = 15.9 Hz, 1H, 2/2'-H), 3.81 (s, 3H, 7'/7-H), 3.80 (s, 3H, 7/7'-H). **¹³C NMR (75 MHz, CDCl₃)** δ 166.2, 166.2, 139.9, 137.4, 134.8, 131.9 (q, ²*J* = 33.0 Hz), 128.2, 126.3 (q, ³*J* = 3.6 Hz), 124.5 (q, ³*J* = 3.8 Hz), 123.7, 123.5 (q, ¹*J* = 272.6 Hz), 123.2, 51.9, 51.9. **MS (EI)** *m/z* = 287 (17 %), 214 (93 %), 186 (58 %), 161 (100 %), 114 (12 %). **HRMS (EI)** *m/z* calcd for C₁₅H₁₃FO₄ [M]⁺: 314.0766, found 214.0772. **IR**, ν 2954 (w), 1705 (s), 1334 (m), 1280 (m), 1113 (s). **mp** 100-103°C.



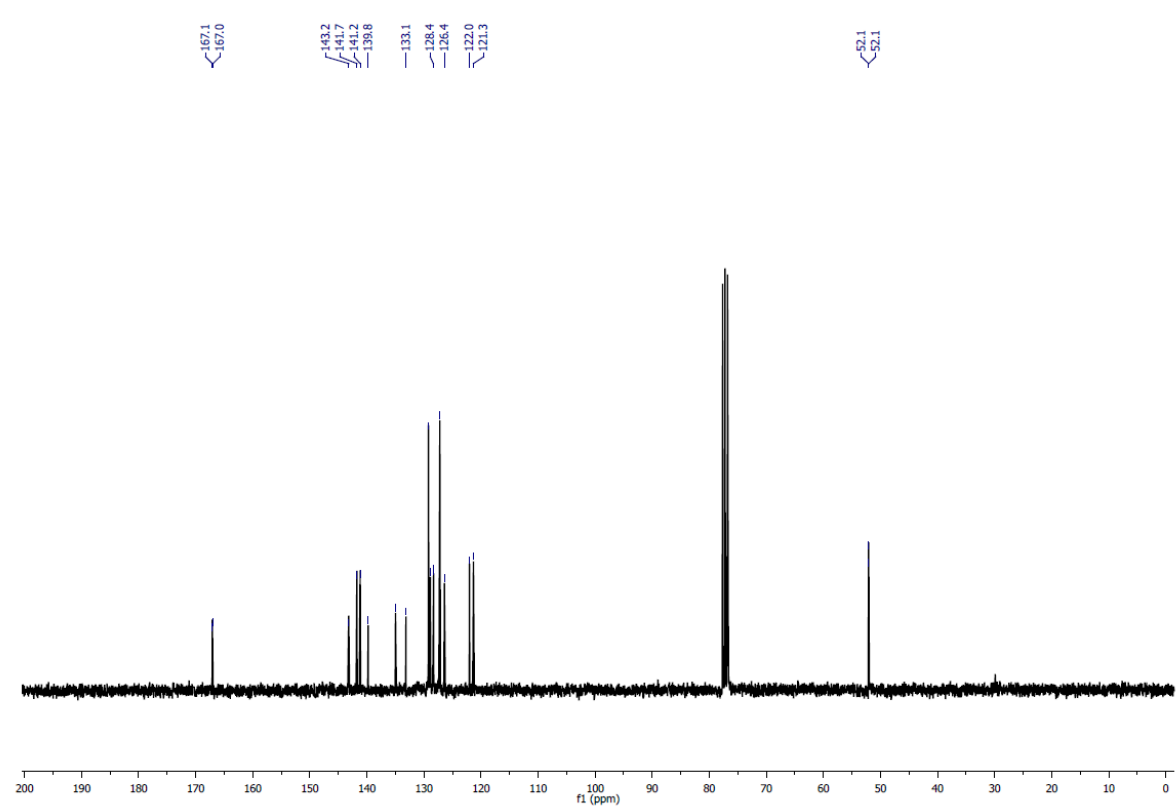
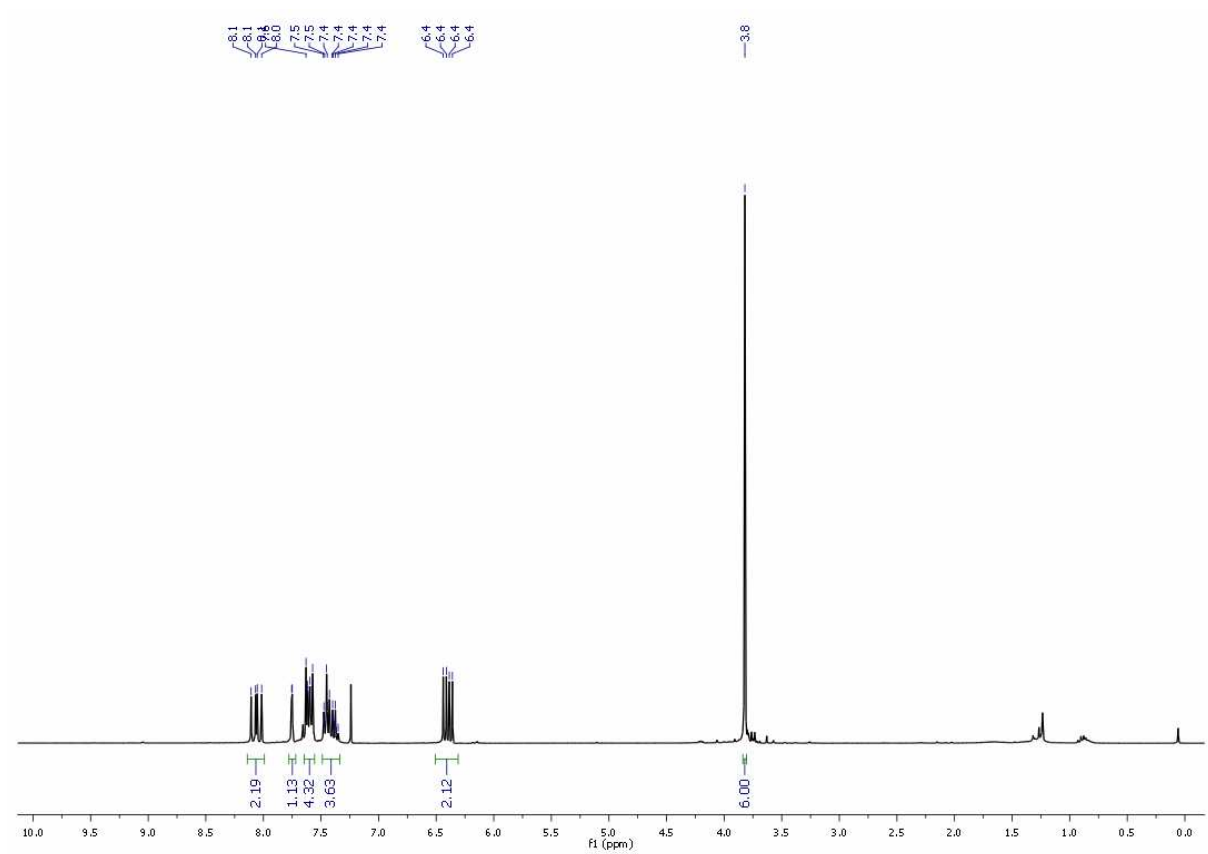
(2*E*, 2'*E*)-Dimethyl 3,3'-biphenyl-3,4-diyl)diacrylate (**4i**)



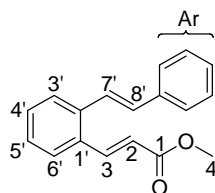
Following the general procedure (method A), (**2*E*, 2'*E***)-dimethyl 3,3'-biphenyl-3,4-diyl)diacrylate (**4i**) was obtained from (*E*)-3-(3-methoxy-3-oxoprop-1-enyl)biphenyl-4-diazonium tetrafluoroborat (**3i**) (0.29 mmol, 100 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 15:1) to afford **4i** as a colourless solid (52 %, 0.15 mmol, 49 mg).

Following the general procedure (method B), (**2*E*, 2'*E***)-dimethyl 3,3'-biphenyl-3,4-diyl)diacrylate (**4i**) was obtained from (*E*)-methyl 3-(4-acetamidobiphenyl-3-yl)acrylate (**2i**) (0.34 mmol, 100 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 15:1) to afford **4i** as a colourless solid (57 %, 0.19 mmol, 62 mg).

¹H NMR (300 MHz, CDCl₃) δ 8.08 (d, *J*= 15.8 Hz, 1H, 3'-H/ 3-H), 8.04 (d, *J*= 15.8 Hz, 1H, 3-H/ 3'-H), 7.75 (d, *J*= 1.6 Hz, 1H, 5-H), 7.65-7.55 (4H, Ar-H), 7.5-7.33 (3H, Ar-H), 6.41 (d, *J*= 15.8 Hz, 1H, 2'-H/ 2-H), 6.39 (d, *J*= 15.8 Hz, 1H, 2-H/ 2'-H), 3.81 (s, 6H, -H). **¹³C NMR (75 MHz, CDCl₃)** δ 167.1, 166.9, 143.2, 141.7, 141.2, 139.8, 134.9, 133.1, 129.2, 128.9, 128.4, 128.3, 127.2, 126.4, 122.0, 121.3, 52.1, 52.1. **MS (EI)** *m/z* = 322 (20 %), 262 (100 %), 231 (95 %), 204 (64 %), 101 (18 %). **HRMS (EI)** *m/z* calcd for C₂₀H₁₈NO₄ [M]⁺: 322.1205, found 322.1208. **Anal.** calcd for C₂₀H₁₈O₄: C, 74.52 %; H, 5.63 % found C, 74.2 %; H, 5.9 %. **IR**, ν 2950 (w), 1712 (s), 1434 (m), 1272 (m), 1168 (s). **mp** 115-118°C.



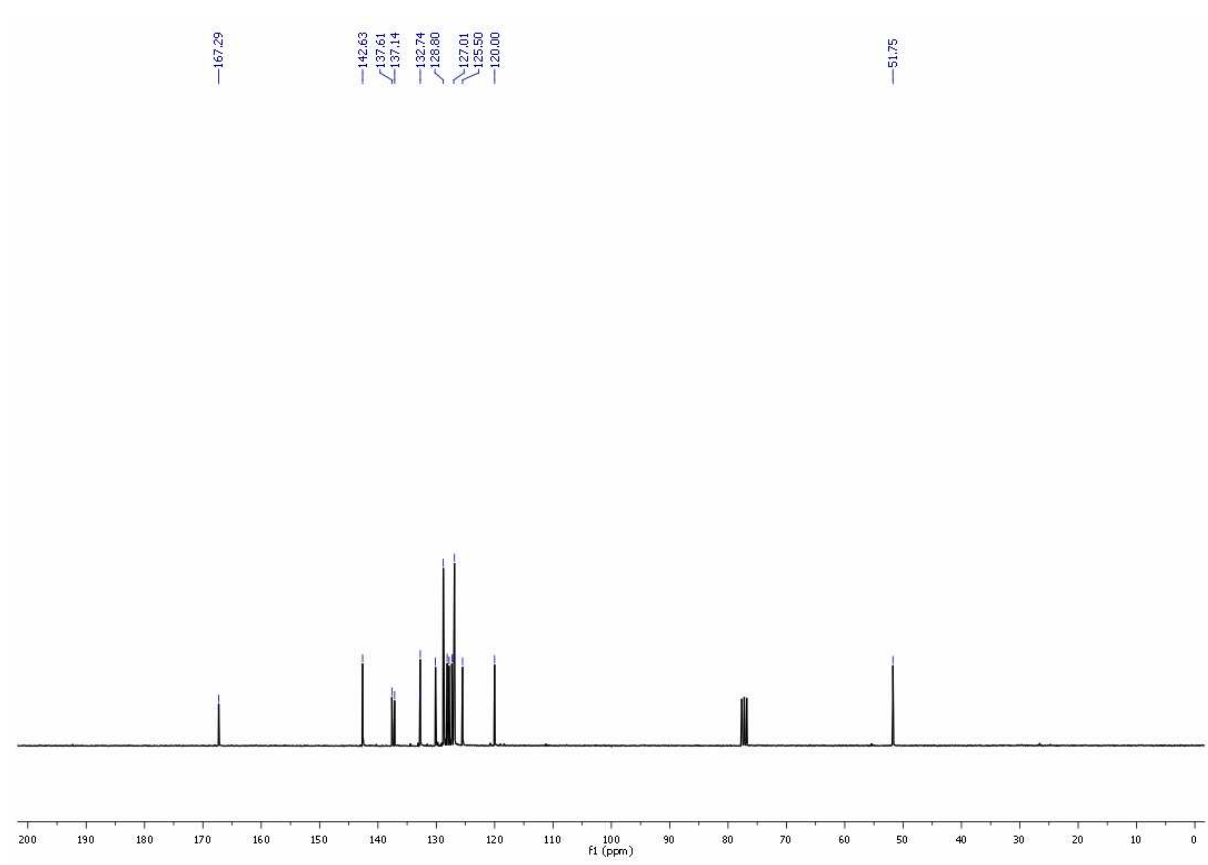
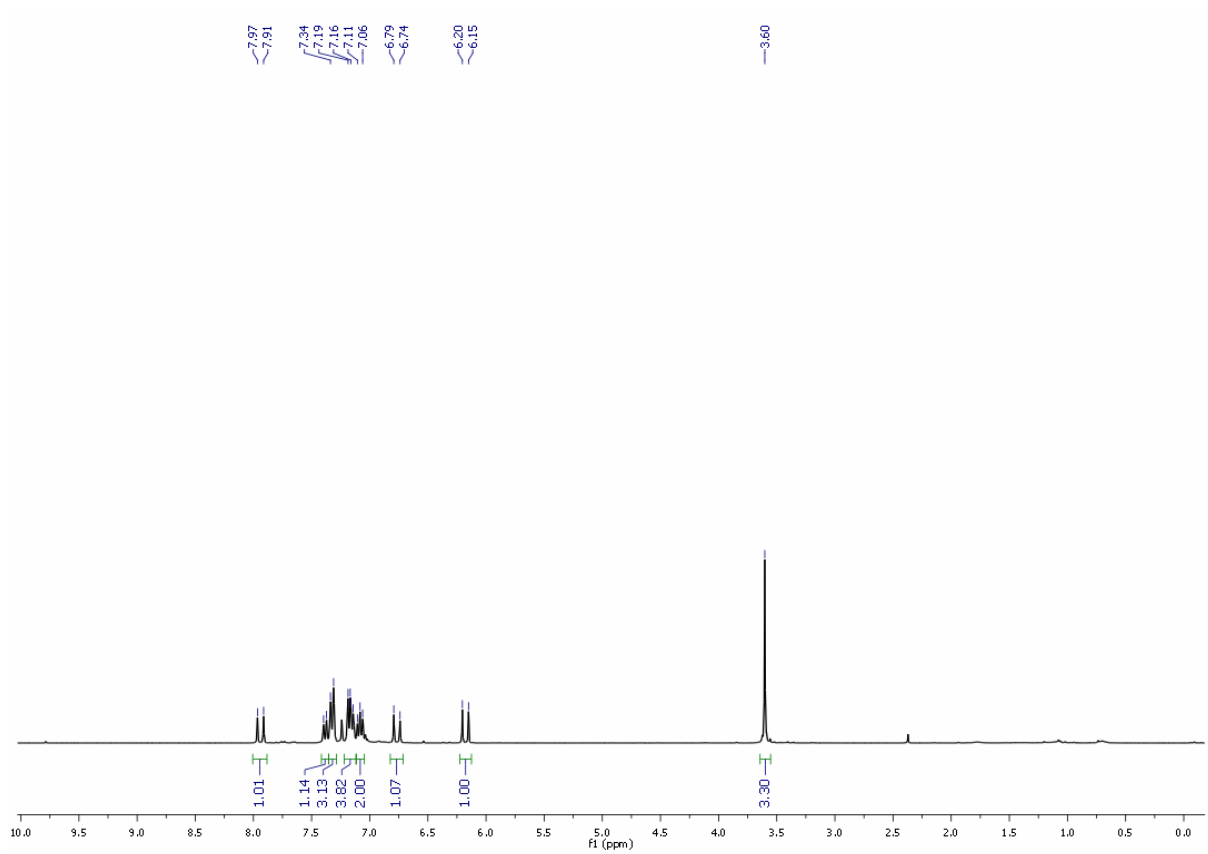
(*E*)-Methyl 3-(2-(*E*)-styrylphenyl)acrylate (**4ab**)



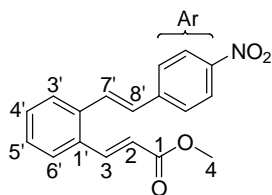
Following the general procedure (method A), (*E*)-methyl 3-(2-(*E*)-styrylphenyl)acrylate (**4ab**) was obtained from (*E*)-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborate (**3a**) (0.5 mmol, 134 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 12:1) to afford **4ab** as a yellow oil (68 %, 0.34 mmol, 90 mg).

Following the general procedure (method B), (*E*)-methyl-3-(2(*E*)-4-nitrostyryl)phenyl)acrylate (**4ab**) was obtained from (*E*)-methyl 3-(2-acetamidophenyl)acrylate (**2a**) (1.0 mmol, 219 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 6:1) to afford **4ab** as a colourless solid (66 %, 0.66 mmol, 175 mg).

¹H NMR (300 MHz, CDCl₃) δ 8.14 (d, *J* = 15.9 Hz, 1H, 3-H), 7.59 (d, *J* = 7.7 Hz, 1H, 6'/3'-H), 7.56-7.49 (3H, Ar-H), 7.42 (d, *J* = 16.2 Hz, 1H, 7'-H), 7.42-7.33 (3H, Ar-H), 7.32-7.25 (2H, Ar-H), 6.97 (d, *J* = 16.1 Hz, 1H, 8'-H), 6.38 (d, *J* = 15.8 Hz, 1H, 2-H), 3.81 (s, 3H, 4-H). **¹³C NMR (75 MHz, CDCl₃)** δ 167.3, 142.6, 137.6, 137.1, 132.8, 132.7, 130.1, 128.8, 128.1, 127.8, 127.3, 127.0, 126.9, 125.5, 120.0, 51.7. **MS (EI)** *m/z* = 264 (46 %), 232 (26 %), 205 (100 %), 127 (13 %), 91 (28 %). **HRMS (EI)** *m/z* calcd for C₁₈H₁₆O₂ [M]⁺: 264.1150, found 264.1158.



(*E*)-Methyl-3-(2(*E*)-4-nitrostyryl)phenyl)acrylat (**4ac**)



Following the general procedure (method A), (*E*)-methyl-3-(2(*E*)-4-nitrostyryl)phenyl)acrylat (**4ac**) was obtained from (*E*)-2-(3-methoxy-3-oxoprop-1-enyl)benzenediazonium tetrafluoroborat (**3a**) (1.0 mmol, 267 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 6:1) to afford **4ac** as a colourless solid (76 %, 0.76 mmol, 235 mg).

Following the general procedure (method B), (*E*)-methyl-3-(2(*E*)-4-nitrostyryl)phenyl)acrylat (**4ac**) was obtained from (*E*)-methyl 3-(2-acetamidophenyl)acrylate (**2a**) (1.0 mmol, 219 mg). The residue was purified by column chromatography (SiO₂, *n*-hexane/methyl tert-butyl ether 6:1) to afford **4ac** as a yellow solid (34 %, 0.34 mmol, 105 mg).

¹H NMR (300 MHz, CDCl₃) δ 8.21 (d, *J* = 8.8 Hz, 2H, 3'-H, 6'-H), 8.08 (d, *J* = 15.8 Hz, 1H, 7'/3-H), 7.65-7.52 (4H, Ar-H), 7.55 (d, *J* = 16.1 Hz, 1H, 3/7'-H), 7.40 (dt, *J* = 3.8, 7.6 Hz, 1H, 5'/4'-H), 7.34 (dt, *J* = 3.9, 7.5 Hz, 1H, 4'/5'-H), 7.00 (d, *J* = 16.1 Hz, 1H, 2/8'-H), 6.37 (d, *J* = 15.8 Hz, 1H, 8'/2-H), 3.80 (s, 3H, -H). **¹³C NMR (75 MHz, CDCl₃)** δ 167.1, 147.1, 143.4, 142.1, 136.3, 133.3, 130.2, 130.1, 130.0, 128.8, 127.5, 127.2, 127.1, 124.2, 120.7, 51.8. **MS (EI)** *m/z* = 309 (20 %), 250 (49 %), 202 (100 %), 128 (23 %), 101 (20 %). **HRMS (EI)** *m/z* calcd for C₁₈H₁₅NO₄ [M]⁺: 309.1001, found 309.1014. **Anal.** calcd for C₁₈H₁₅NO₄: C, 69.9 %; H, 4.9 %; N, 4.5 % found C, 70.0 %; H, 4.6 %; N, 4.4 %. **IR** ν 2950 (w), 1712 (m), 1513 (m), 1338 (s), 1172 (m). **mp** 130°C.

