

## Supplementary information

### Functionalized alkoxy arene diazonium salts from Paracetamol

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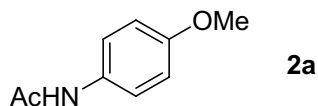
***CAUTION: Although spontaneous combustion or even explosions were never observed in our laboratory upon synthesizing or handling the arene diazonium salts described herein, we recommend to handle these compounds with care. In particular, the mmol-scale should not be exceeded when standard laboratory conditions are used, and heating or melting of the pure substances should be avoided.***

## A General Remarks

All experiments were conducted in dry reaction vessels under an atmosphere of dry argon. Solvents were purified by standard procedures.  $^1\text{H}$  NMR spectra were obtained at 300 MHz, 400 MHz, or 500 MHz in  $\text{CDCl}_3$  with  $\text{CHCl}_3$  ( $\delta = 7.26$  ppm) as an internal standard. Coupling constants ( $J$ ) are given in Hz.  $^{13}\text{C}$  NMR spectra were recorded at 75 MHz, 100 MHz, or 125 MHz in  $\text{CDCl}_3$  with  $\text{CDCl}_3$  ( $\delta = 77.0$  ppm) as an internal standard. Whenever the solubility of the sample was insufficient in  $\text{CDCl}_3$ , one of the following solvents was used for NMR-measurements:  $\text{DMSO-d}^6$  ( $\text{DMSO-d}^5$  as internal standard for  $^1\text{H}$ -NMR-spectroscopy with  $\delta = 2.50$ ,  $\text{DMSO-d}^6$  as internal standard for  $^{13}\text{C}$ -NMR-spectroscopy with  $\delta = 39.5$  ppm);  $\text{CD}_3\text{OD}$  ( $\text{CD}_2\text{HOD}$  as internal standard for  $^1\text{H}$ -NMR-spectroscopy with  $\delta = 3.31$ ,  $\text{CD}_3\text{OD}$  as internal standard for  $^{13}\text{C}$ -NMR-spectroscopy with  $\delta = 49.2$  ppm);  $\text{CD}_3\text{C(O)CD}_3$  ( $\text{CD}_2\text{HC(O)CD}_3$  as internal standard for  $^1\text{H}$ -NMR-spectroscopy with  $\delta = 2.05$ ,  $\text{CD}_3\text{C(O)CD}_3$  as internal standard for  $^{13}\text{C}$ -NMR-spectroscopy with  $\delta = 29.9$  ppm). Whenever signal assignments in  $^1\text{H}$ - or  $^{13}\text{C}$ -NMR spectra are given, these are based on H,H- and H,C-correlation spectroscopy, and NOE-spectroscopy if necessary. IR spectra were recorded as films on NaCl or KBr plates or as KBr-discs. Wavenumbers ( $\nu$ ) are given in  $\text{cm}^{-1}$ . The peak intensities are defined as strong (s), medium (m) or weak (w). Mass spectra were obtained at 70 eV. Whenever known compounds were used as starting materials, reagents or catalysts, they were either purchased or were synthesized following literature procedures, which are cited in the appropriate section.

## B Experimental procedures, analytical data and copies of spectra for aromatic acetamides 2

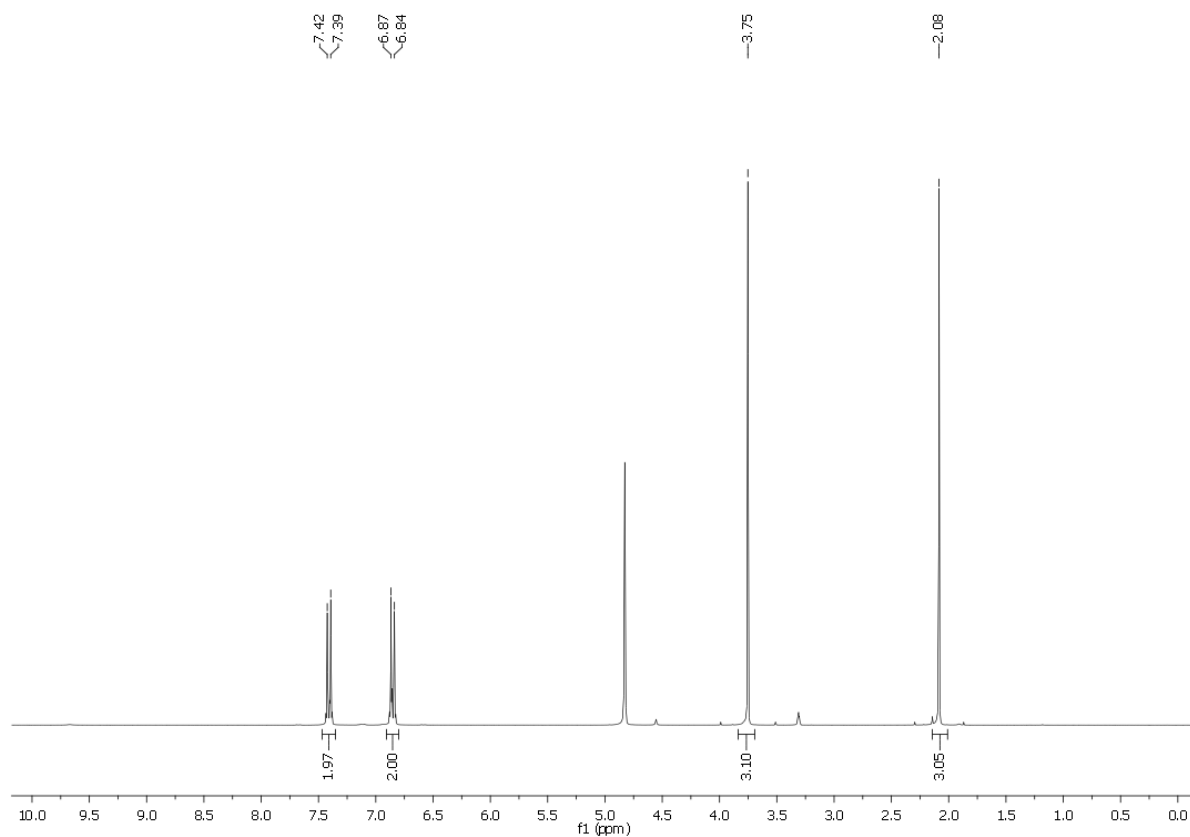
### B1 4-Methoxyacetanilide (**2a**)<sup>1</sup>



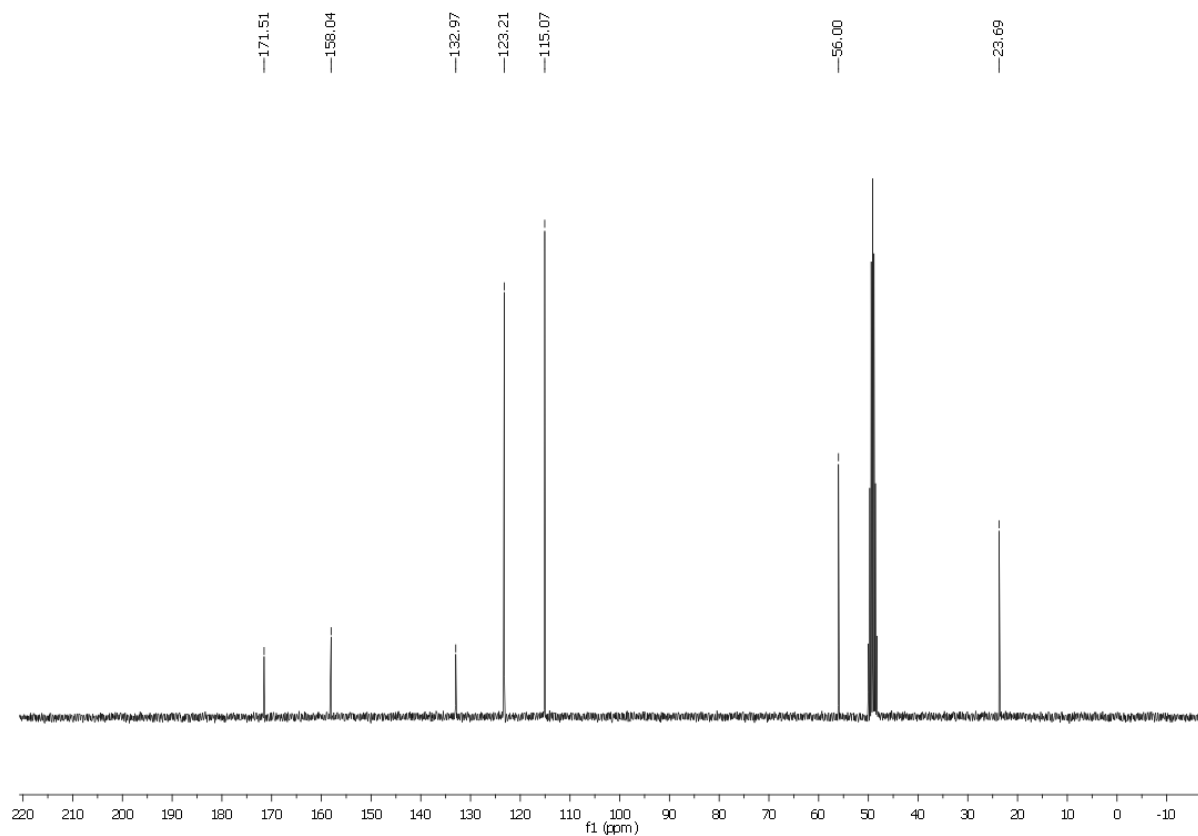
The title compound was purchased. Alternatively, it can be easily synthesized from 4-acetamidophenol: 4-Acetamidophenol (**1**) (33.1 mmol, 5.00 g), K<sub>2</sub>CO<sub>3</sub> (50.0 mmol, 6.60 g) and methyl iodide (49.6 mmol, 7.04 g, 3.10 mL) in dry acetone (100 mL) were heated to reflux for 24 hours. The solution was concentrated in vacuum, and the residue partitioned in ethyl acetate and water. The aqueous layer was extracted three times with ethyl acetate (20 mL each). The combined organic layers were dried with MgSO<sub>4</sub>, filtered, and the solvent was evaporated in vacuum. The residue was chromatographed on silica to give 4-methoxyacetanilide (**2a**) as a colourless solid in quantitative (33.1 mmol, 5.47 g) yield. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ 7.41 (d, *J* = 9.1, 2H), 6.85 (d, *J* = 9.1, 2H), 3.75 (s, 3H), 2.08 (s, 3H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) δ 171.5, 158.0, 133.0, 123.2, 115.1, 56.0, 23.7.

<sup>1</sup> T. Cablewski, P. A. Gurr, K. D. Raner and C. R. Strauss, *J. Org. Chem.*, 1994, **59**, 5814-5817.

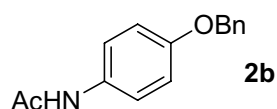
$^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ ):



$^{13}\text{C}$ -NMR (75 MHz,  $\text{CD}_3\text{OD}$ ):



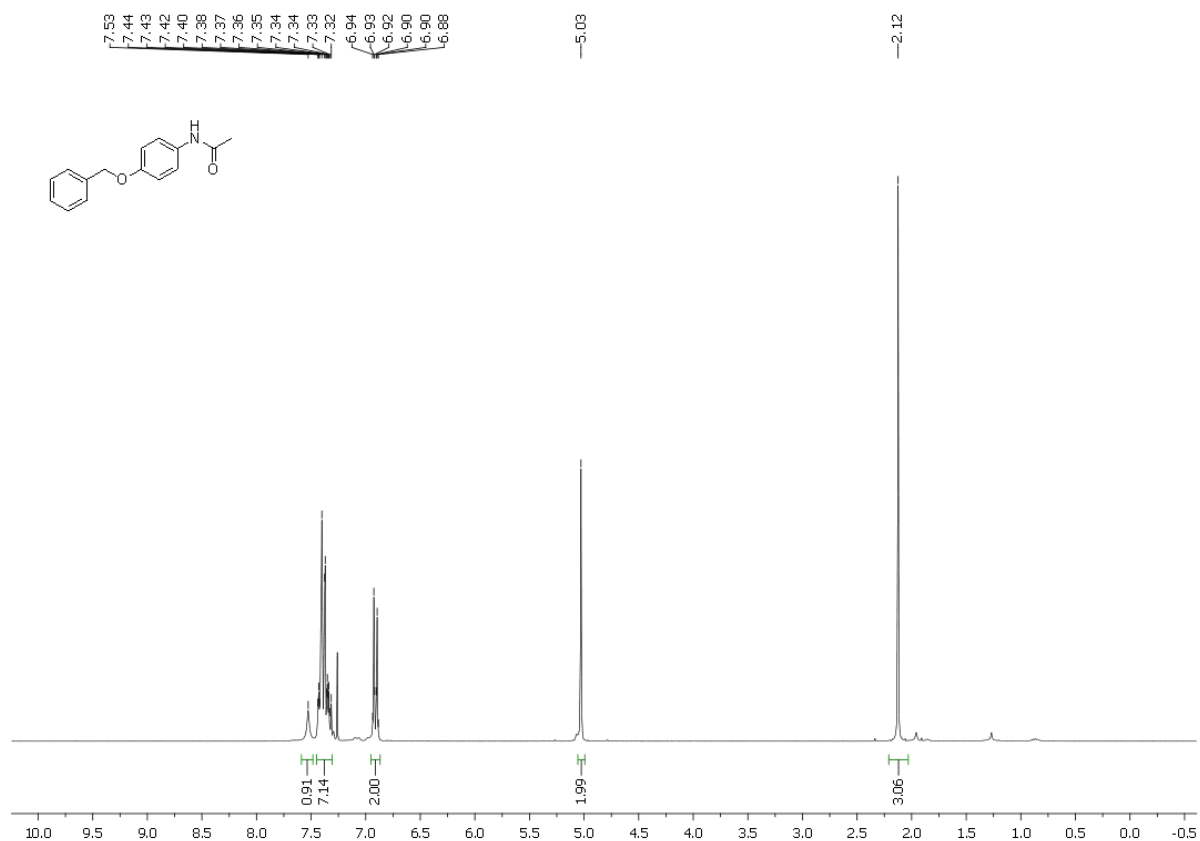
B2 4-Benzoyloxyacetanilide (**2b**)<sup>2</sup>



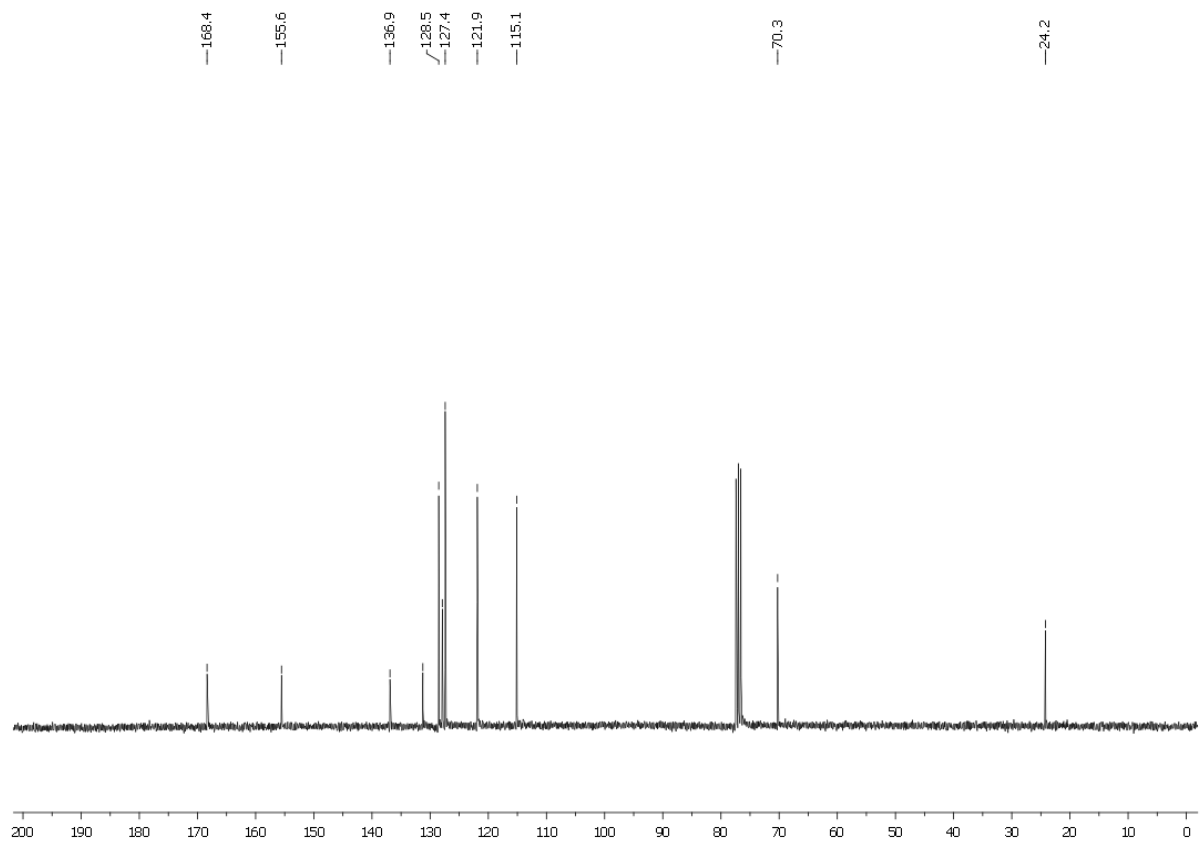
4-Acetamidophenol (**1**) (40.0 mmol, 6.00 g), K<sub>2</sub>CO<sub>3</sub> (50.0 mmol, 6.60 g) and benzyl bromide (44.0 mmol, 7.50 g) in acetone (100 mL) were heated to reflux for four hours. The suspension was filtered and washed with cold MTBE (100 mL). The filtrate was concentrated under reduced pressure to give 4-benzyloxyacetanilide (**2b**) as a pale solid in 97 % (39.0 mmol, 9.30 g) yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.53 (s(br.), 1H), 7.45 – 7.31 (7H), 6.91 (d, J = 8.2, 2H), 5.03 (s, 2H), 2.12 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 168.4, 155.6, 136.9, 131.2, 128.5, 127.9, 127.4, 121.9, 115.1, 70.3, 24.2; LRMS (ESI): *m/z* = 242 (100 %), 200 (24 %); HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>16</sub>NO<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 242.1181; found: 242.1166.

<sup>2</sup> M. Paventi and A. S. Hay, *J. Org. Chem.*, 1991, **56**, 5857-5882.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):

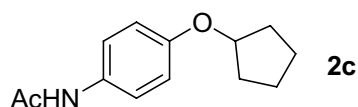


$^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):



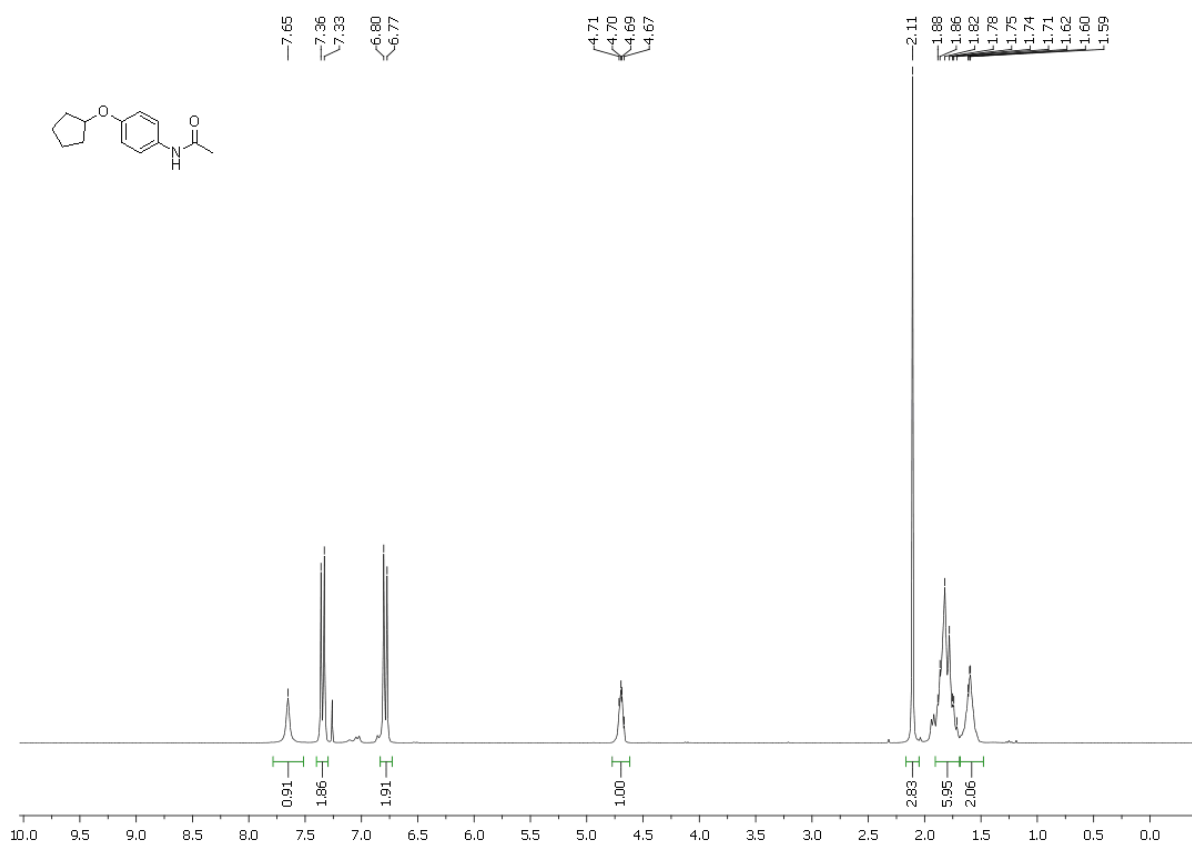


B3 4-Cyclopentyloxyacetamide (**2c**)

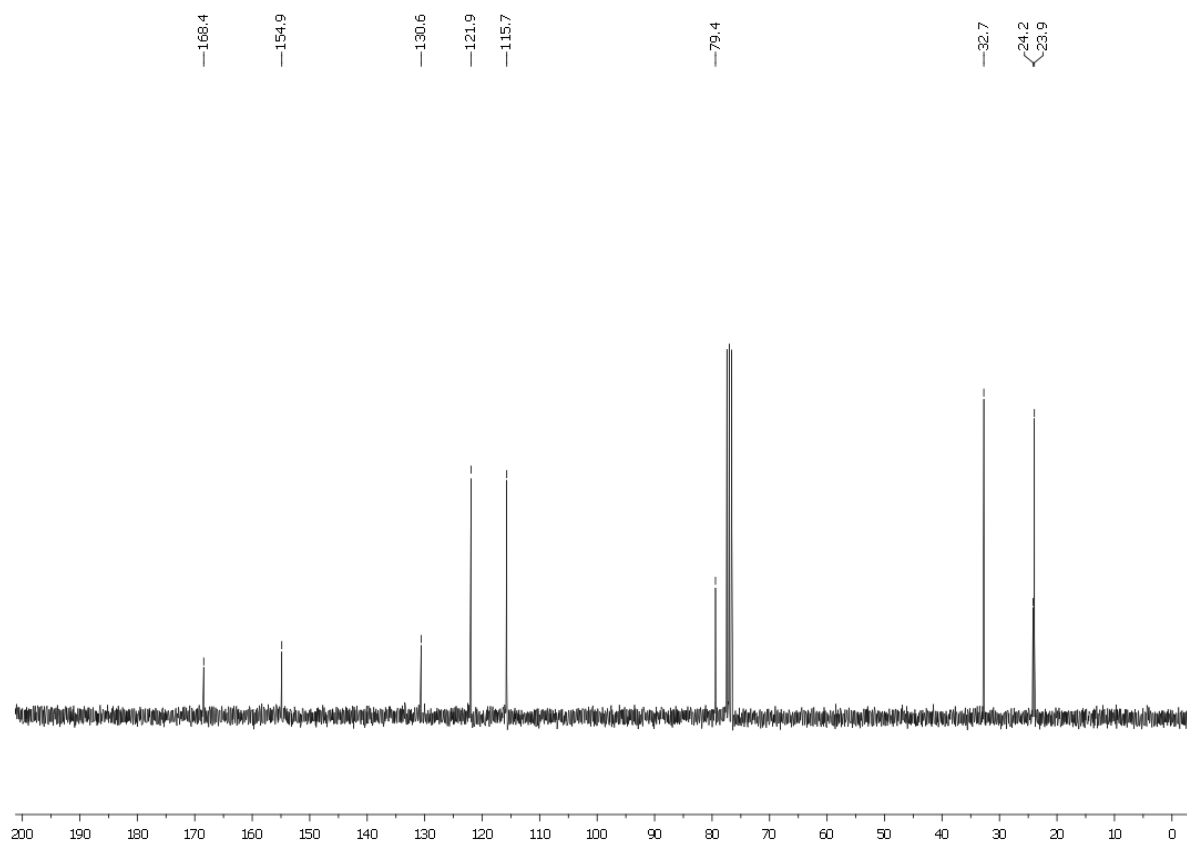


4-Acetamidophenol (**1**) (16.0 mmol, 2.50 g), cyclopentyl bromide (20.0 mmol, 2.90 g),  $K_2CO_3$  (20.0 mmol, 2.70 g) and NaI (0.80 mmol, 120 mg) in acetone (50 mL) were heated to reflux for 24 hours. The suspension was filtered and washed with cold MTBE (100 mL). The filtrate was concentrated under reduced pressure to give a pale residue, which was dissolved in dichloromethane under ultrasonication. The solution was kept at 0°C for 12 hours, which led to crystallization of unreacted 4-acetamidophenol (**1**). The precipitate was filtered and the solution was concentrated to give 4-cyclopentyloxyacetanilide (**2c**) as a pale solid in 70 % (14.0 mmol, 3.00 g) yield, mp 127°C.  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.65 (s(br), 1H), 7.34 (d,  $J = 8.9$ , 2H), 6.79 (d,  $J = 8.9$  Hz, 2H), 4.71 (m, 1H), 2.11 (s, 3H), 1.92 – 1.72 (6H), 1.64 – 1.58 (2H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  168.4, 154.9, 130.6, 121.9, 115.7, 79.4, 32.7, 24.2, 23.9; IR (KBr-disc)  $\nu$  3294 (w), 2961 (w), 1659 (m), 1603 (w), 1544 (m), 1508 (s), 1240 (s); MS (ESI):  $m/z = 220$  (100 %), 152 (74 %). HRMS (ESI)  $m/z$  calcd for  $C_{13}H_{18}NO_2^+$   $[M+H]^+$ : 220.1338; found: 220.1345; Anal. calcd for  $C_{13}H_{17}NO_2$ : C, 71.2 %; H, 7.8 %; N, 6.4 %; found: C, 71.4 %; H, 7.9 %; N, 6.4 %.

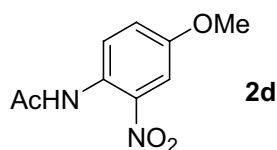
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):



$^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):



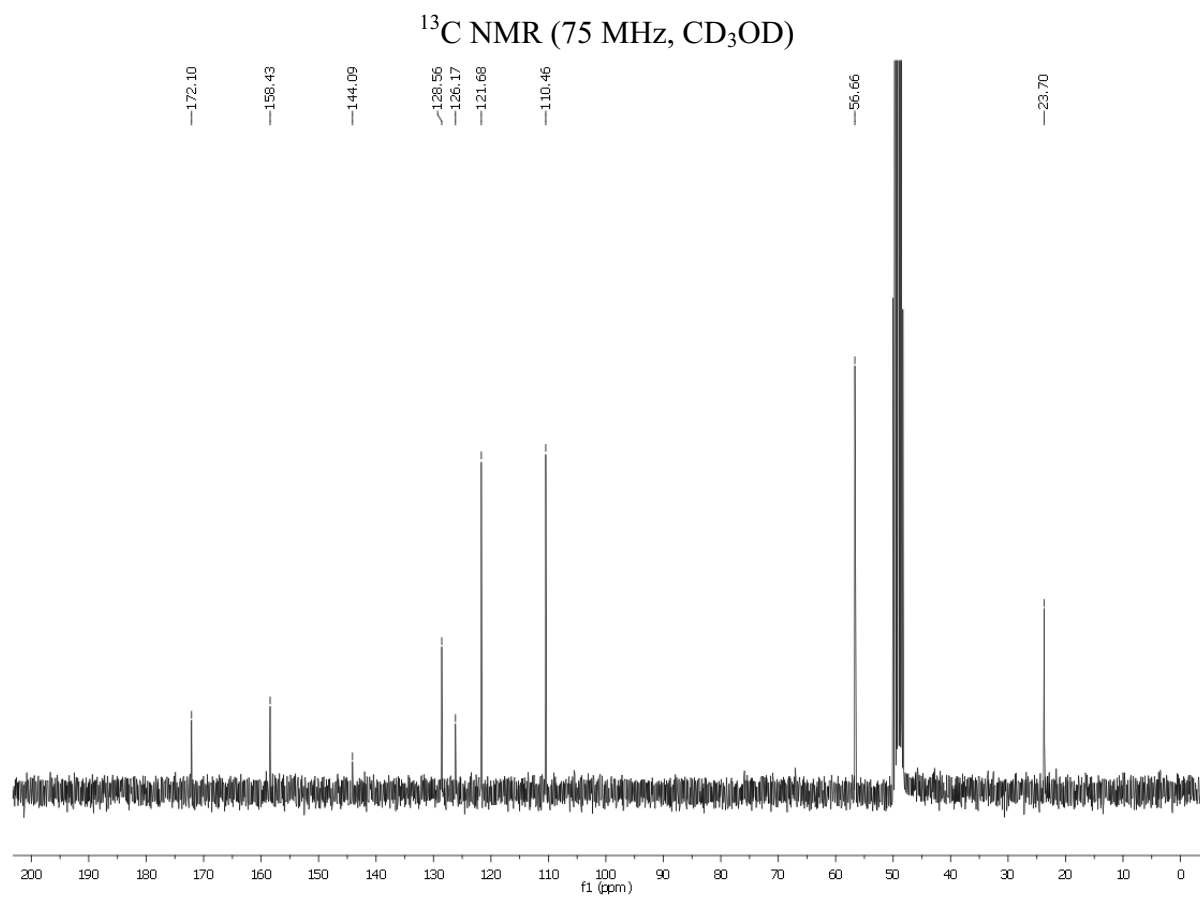
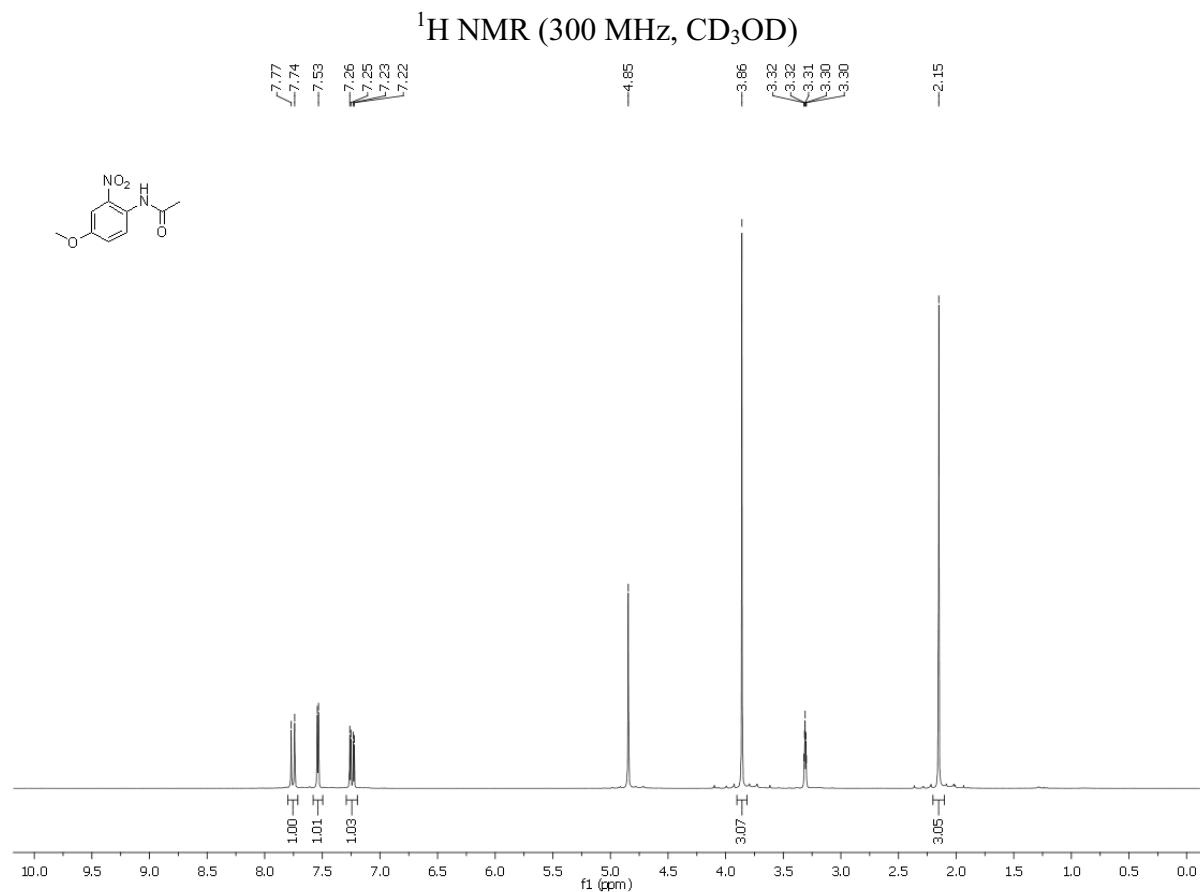
B4 4-Methoxy-2-nitroacetanilide (**2d**)<sup>3</sup>



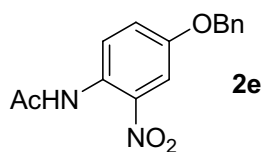
4-Methoxyacetanilide (**2a**) (3.0 mmol, 500 mg) and nitric acid (4.0 mL, 12 %ig) were heated to 50°C for one hour. After ten minutes the colour turned to yellow. The cold solution was treated with ice water (20 mL). The precipitate was filtered and washed with water. The solid was dried under vacuum to give 4-methoxy-2-nitroacetanilide (**2d**) as a yellow solid in 79 % (2.40 mmol, 500 mg) yield, mp 118°C (reported in the literature:<sup>4</sup> 115-119°C). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ 7.76 (d, *J* = 9.0, 1H), 7.54 (d, *J* = 3.0, 1H), 7.24 (dd, *J* = 3.0, 9.0, 1H), 3.86 (s, 3H), 2.15 (s, 3H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) δ 172.1, 158.4, 144.1, 128.6, 126.2, 121.7, 110.5, 56.7, 23.7; IR (KBr-disc) ν 3376 (m), 1698 (s), 1578 (s), 1508 (s), 1314 (s); LRMS (ESI) *m/z* = 151 (8 %), 169 (100 %), 211 (36 %); HRMS (ESI) *m/z* calcd for C<sub>9</sub>H<sub>11</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup> [M+H]<sup>+</sup>: 211.0719, found 211.0715; Anal. calcd for C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>: C, 51.4 %; H, 4.8 %; N, 13.3 %; found C, 51.6 %; H, 4.9 %; N, 13.2 %.

<sup>3</sup> M. Tanno and S. Sueyoshi, *Chem. Pharm. Bull.*, 1987, **35**, 1360-1371.

<sup>4</sup> P. E. Fanta, D. S. Tarbell, *Org. Synth.*, 1955, **Coll. Vol. III**, 661.



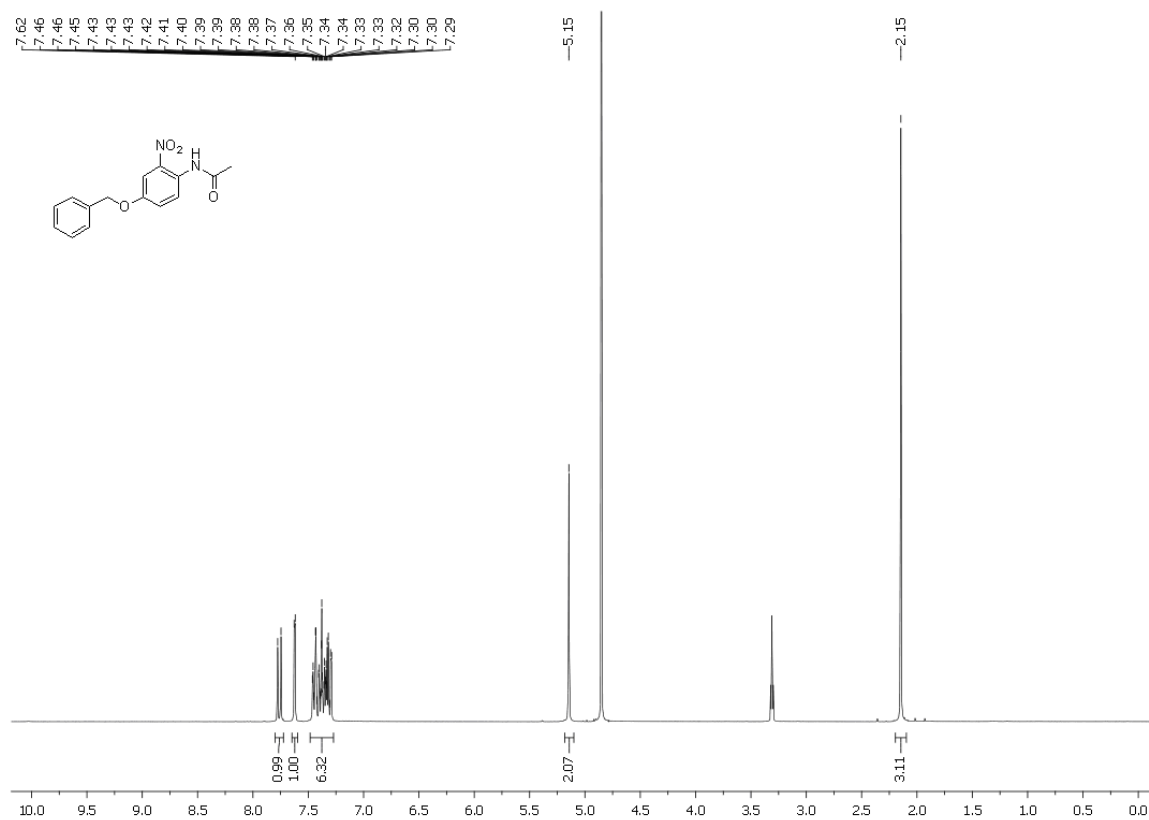
B5 4-Benzyloxy-2-nitroacetanilide (**2e**)<sup>5</sup>



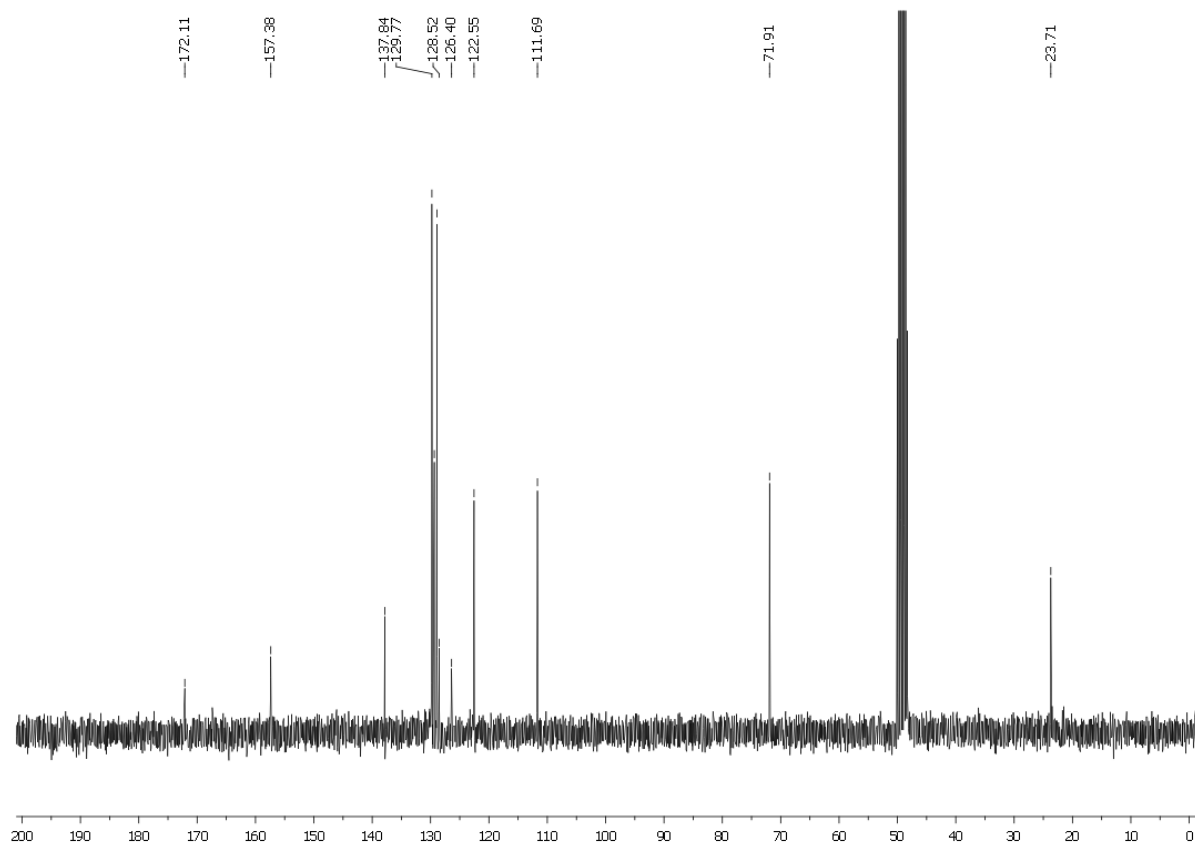
4-Benzyloxyacetanilide (**2b**) (3.0 mmol, 731 mg) and nitric acid (4.0 mL, 12 % solution in water) were heated to 95°C for one hour. After ten minutes the colour turned to yellow. The cold solution was treated with ice water (20 mL). The precipitate was filtered and washed with water. The solid was dried under vacuum to give 4-benzyloxy-2-nitroacetanilide (**2e**) as a yellow solid in 94 % (2.40 mmol, 500 mg) yield, mp 113°C (reported in the literature:<sup>5</sup> 108-114°C). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ 7.76 (d, *J* = 9.0, 1H), 7.63 (d, *J* = 2.9, 1H), 7.49 – 7.27 (6H), 5.15 (s, 2H), 2.15 (s, 3H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) δ 172.1, 157.4, 137.9, 129.8, 129.4, 128.9, 128.5, 126.4, 122.6, 111.7, 71.9, 23.7; IR (KBr-disc) ν 3347 (m), 1698 (s), 1503 (s), 1306 (s), 1270 (s); MS (ESI) *m/z* = 199 (7 %), 245 (100 %), 287 (46 %); HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>15</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup> [M+H]<sup>+</sup>: 287.1032, found 287.1050; Anal. calcd for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>: C, 62.9 %; H, 4.9 %; N, 9.8 %; found C, 62.4 %; H, 4.8 %; N, 9.6 %.

<sup>5</sup> W. Wiegrebe, L. Faber and H. Budzikiewicz, *Liebigs Ann. Chem.*, 1970, **733**, 125-140.

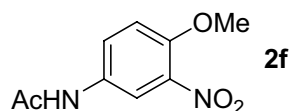
$^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ )



$^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{OD}$ )



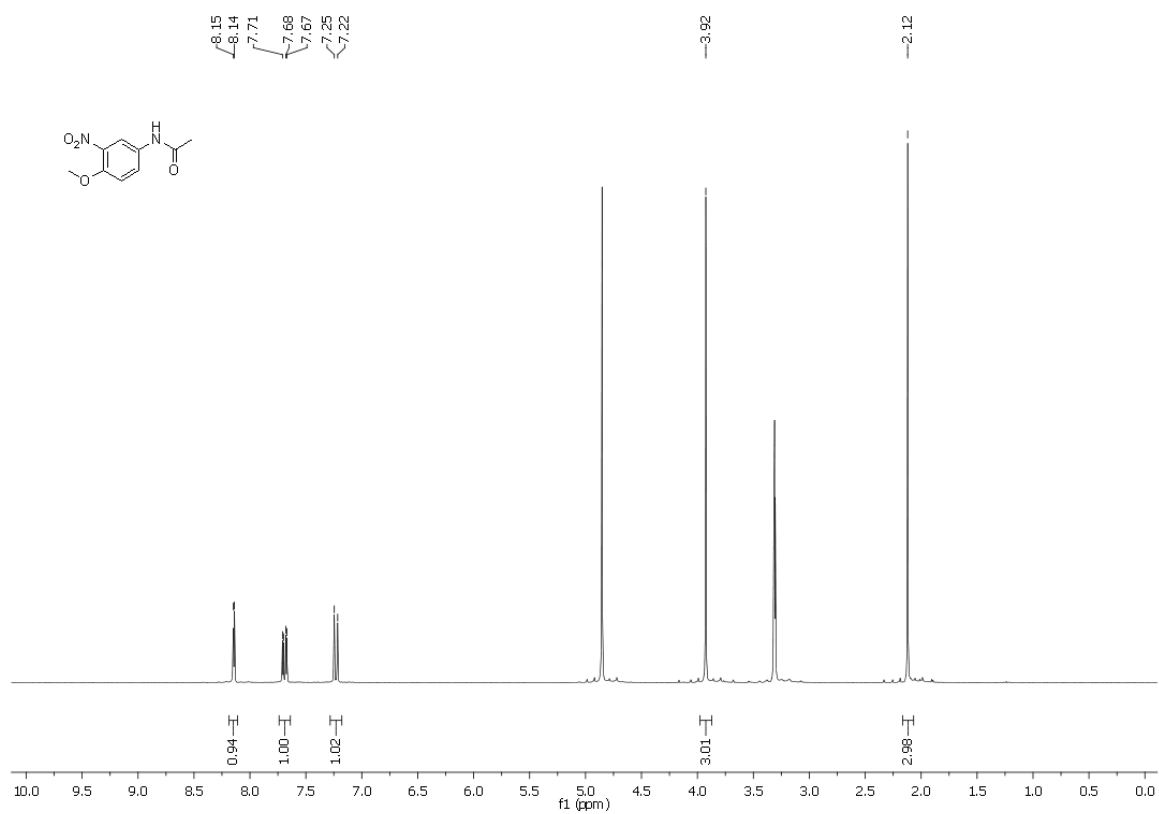
B6 4-Methoxy-3-nitroacetanilide (**2f**)<sup>6</sup>



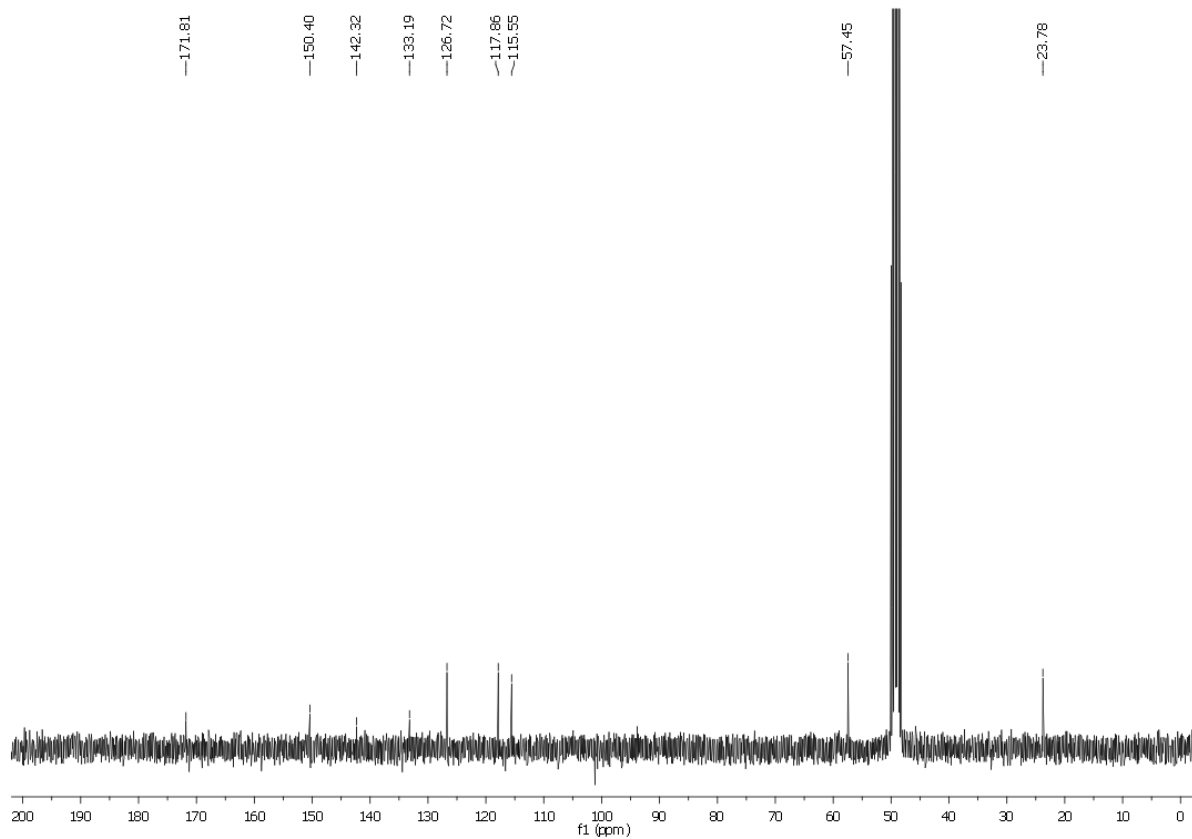
4-Methoxyacetanilide (**2a**) (3.0 mmol, 500 mg) was slowly added at 0°C to sulfuric acid (5 mL 85 %) and stirred until the solid was completely dissolved. Guanidinium nitrate (3.0 mmol, 370 mg) was added to the reaction mixture over a period of 30 minutes. After stirring for three hours at 0-5°C, the solution was treated with ice water (20 mL). The precipitate was dissolved in EtOAc. The aqueous layer was extracted three times with EtOAc (10 mL each). The combined organic layers were dried with MgSO<sub>4</sub>, and the solvent was evaporated in vacuum. The residue was purified by column chromatography (SiO<sub>2</sub>, EtOAc:MTBE 1:1) to give 4-methoxy-3-nitroacetanilide (**2f**) as a yellow solid in 82 % (2.49 mmol, 520 mg) yield, mp 151°C (reported in the literature:<sup>6</sup> 148-153°C). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ 8.14 (d, *J* = 2.7, 1H), 7.69 (dd, *J* = 2.7, 9.1, 1H), 7.23 (d, *J* = 9.1, 1H), 3.92 (s, 3H), 2.12 (s, 3H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) δ 171.8, 150.4, 142.3, 133.2, 126.7, 117.9, 115.6, 57.5, 23.8; IR (KBr-disc) ν 3372 (m), 1684 (s), 1536 (s), 1323 (s), 1250 (s); MS (ESI) *m/z* = 99 (4 %), 165 (4 %), 211 (100 %); HRMS (ESI) *m/z* calcd for C<sub>9</sub>H<sub>11</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup> [M+H]<sup>+</sup>: 211.0719, found 211.0720; Anal. calcd for C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>: C, 51.4 %; H, 4.8 %; N, 13.3 %; found C, 51.2 %; H, 4.8 %; N, 13.3 %.

<sup>6</sup> M. M. V. Ramana, S. S. Malik and J. A. Parihar, *Tetrahedron Lett.*, 2004, **45**, 8681-8683.

$^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ )

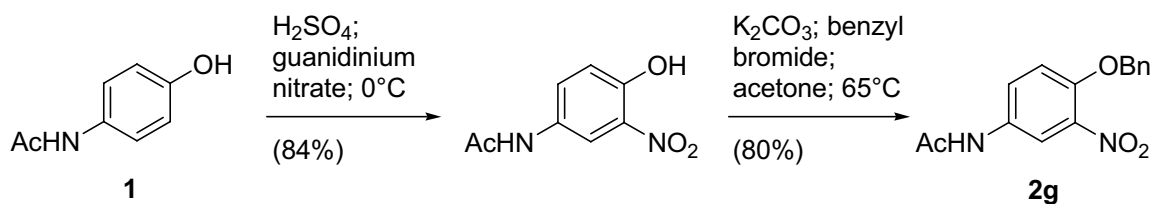


$^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{OD}$ )





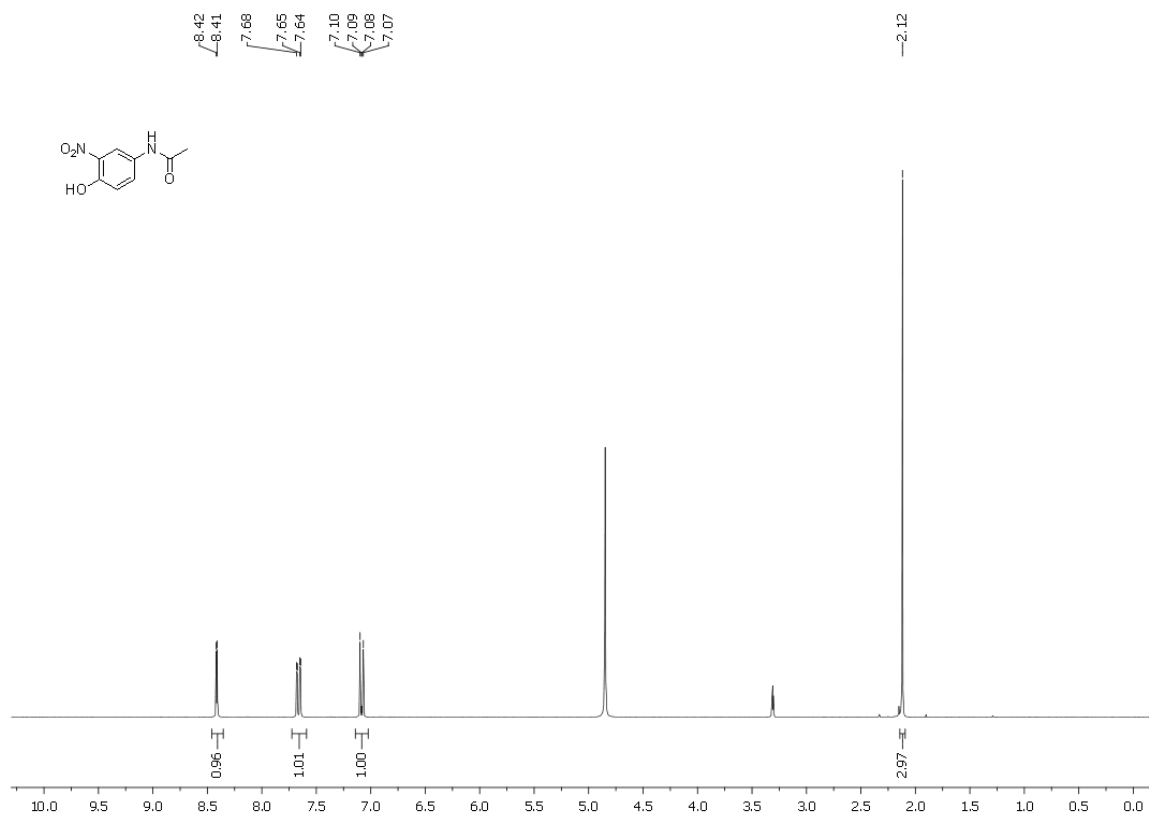
B7 4-Benzyloxy-3-nitroacetanilide (**2g**)



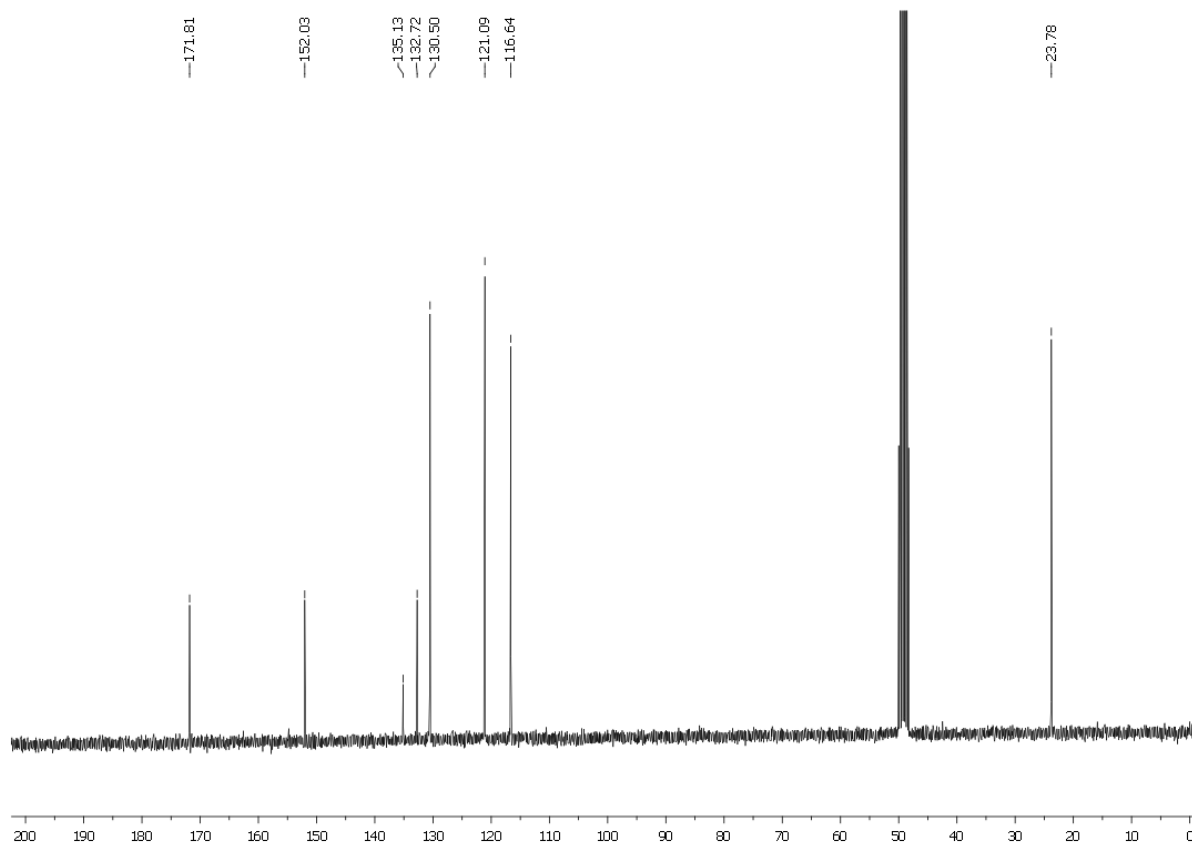
**4-Hydroxy-3-nitroacetanilide:** 4-Hydroxyacetanilide (**1**) (66.2 mmol, 10.00 g) was slowly added to ice-cold sulfuric acid (50 mL, 85 % aqueous solution) and stirred until the solid was dissolved. Guanidinium nitrate (69.5 mmol, 8.50 g) was then added to the reaction mixture over a period of 30 minutes. After stirring for three hours at 0-5°C ice water (100 mL) was slowly added. The precipitate was dissolved in EtOAc, and the aqueous layer was extracted three times with EtOAc (30 mL each). The combined organic extracts were dried with MgSO<sub>4</sub> and evaporated in vacuum. The residue was purified by column chromatography (SiO<sub>2</sub>, MTBE) to give 4-hydroxy-3-nitroacetanilide as a yellow solid in 84 % (55.6 mmol, 10.00 g) yield, mp 158°C (reported in the literature:<sup>7</sup> 154°C-162°C). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ 8.43 (d, *J* = 2.6, 1H), 7.68 (dd, *J* = 2.7, 9.0, 1H), 7.10 (d, *J* = 9.0, 1H), 2.12 (s, 3H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) δ 171.8, 152.1, 135.1, 132.7, 130.5, 121.1, 116.7, 23.8; IR (KBr-disc) ν 3283 (m), 1659 (s), 1537 (s), 1480 (s), 1269 (s); MS (EI) *m/z* = 80 (41 %), 119 (53 %), 196 (100 %); HRMS (EI) *m/z* calcd for C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup> [M]<sup>+</sup>: 196.0484, found 196.0496; Anal. calcd for C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>: C, 49.0 %; H, 4.1 %; N, 14.3 %; found C, 49.0 %; H, 4.1 %; N, 14.2 %.

<sup>7</sup> M. Rapoport, C. K. Hancock and E. A. Meyers, *J. Am. Chem. Soc.*, 1961, **83**, 3489-3494.

$^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ )

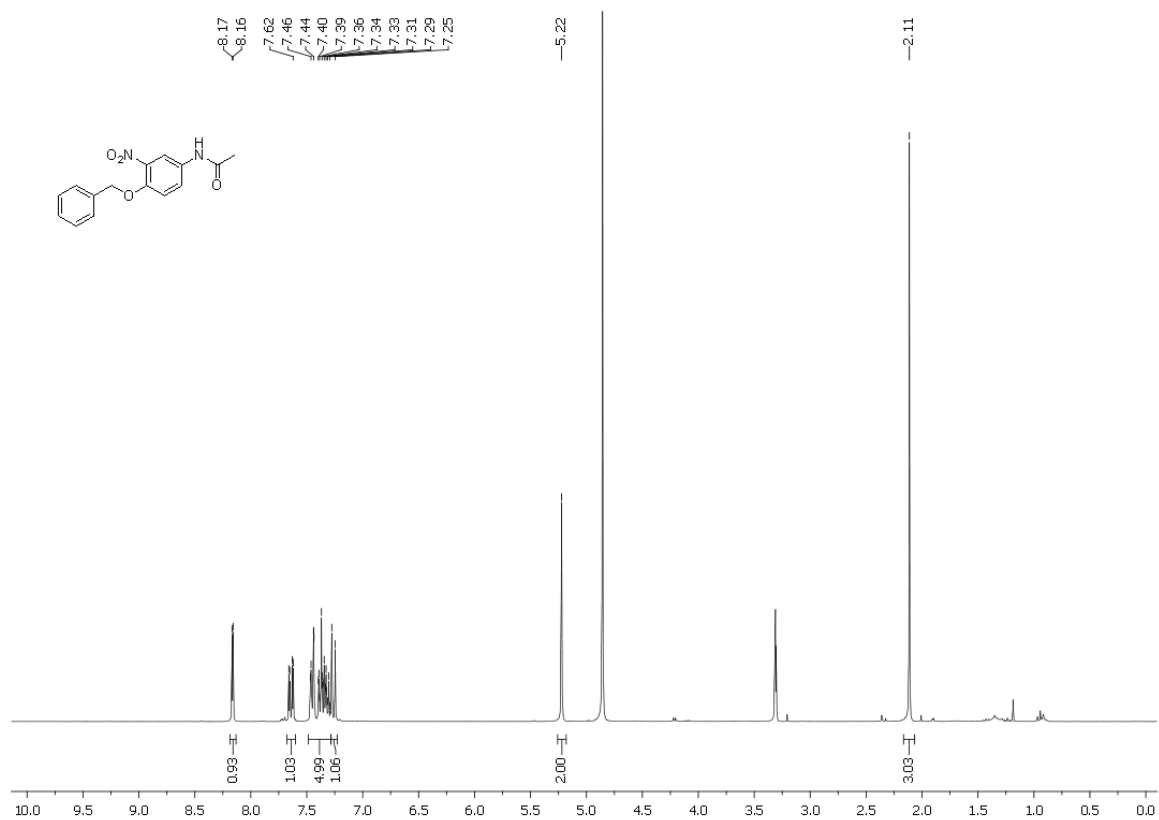


$^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{OD}$ )

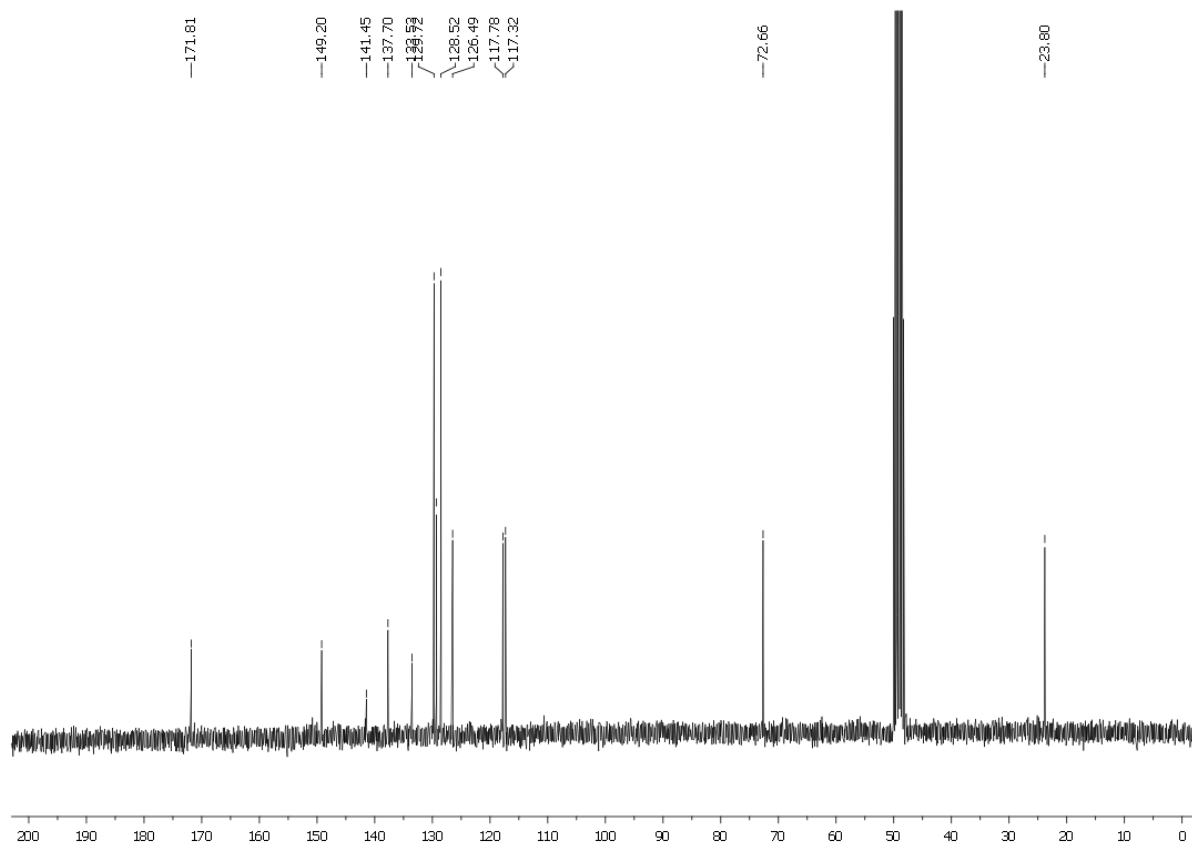


**4-Benzyloxy-3-nitroacetanilide (2g):** 4-Hydroxy-3-nitroacetanilide (10.2 mmol, 2.00 g),  $K_2CO_3$  (13.3 mmol, 1.80 g) and benzyl bromide (13.3 mmol, 2.30 g, 1.60 mL) in acetone (100 mL) were heated to reflux for six hours and then stirred at room temperature for 12 hours. The solution was concentrated in vacuum, and the residue dissolved with EtOAc and water. The aqueous layer was extracted three times with EtOAc (30 mL each). The combined organic layers were dried with  $MgSO_4$  and evaporated in vacuum. The residue was purified by column chromatography ( $SiO_2$ , EtOAc:MTBE 1:2) to give 4-benzyloxy-3-nitroacetanilide (**2g**) as a yellow solid in 80 % (8.2 mmol, 2.30 g) yield, mp 124°C.  $^1H$  NMR (300 MHz,  $CD_3OD$ )  $\delta$  8.16 (d,  $J = 2.7$ , 1H), 7.64 (dd,  $J = 2.7, 9.1$ , 1H), 7.48 – 7.41 (2H), 7.41 – 7.29 (3H), 7.26 (d,  $J = 9.1$ , 1H), 5.22 (s, 2H), 2.11 (s, 3H);  $^{13}C$  NMR (75 MHz,  $CD_3OD$ )  $\delta$  171.8, 149.2, 141.4, 137.7, 133.5, 129.7, 129.3, 128.5, 126.5, 117.8, 117.3, 72.6, 23.8; IR (KBr-disc)  $\nu$  3393 (s), 1685 (s), 1527 (m), 1313 (s); MS (ESI)  $m/z$  287 (10 %), 197 (100 %), 121 (8 %), 99 (20 %); HRMS (ESI)  $m/z$  calcd for  $C_{15}H_{15}N_2O_4^+$   $[M+H]^+$ : 287.1032, found 287.1025; Anal. calcd for  $C_{15}H_{14}N_2O_4$ : C, 62.9 %; H, 4.9 %; N, 9.8 %; found C, 62.9 %; H, 5.0 %; N, 9.6 %.

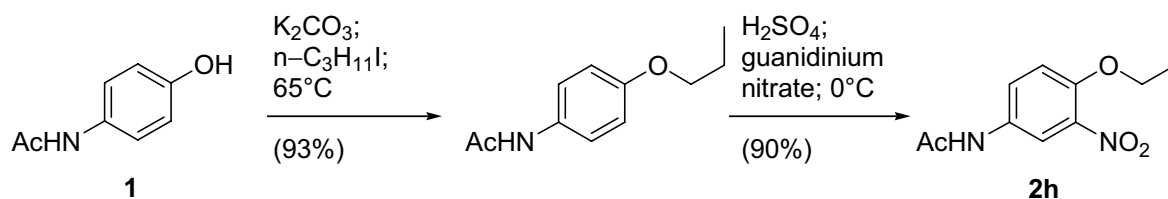
$^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ )



$^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{OD}$ )



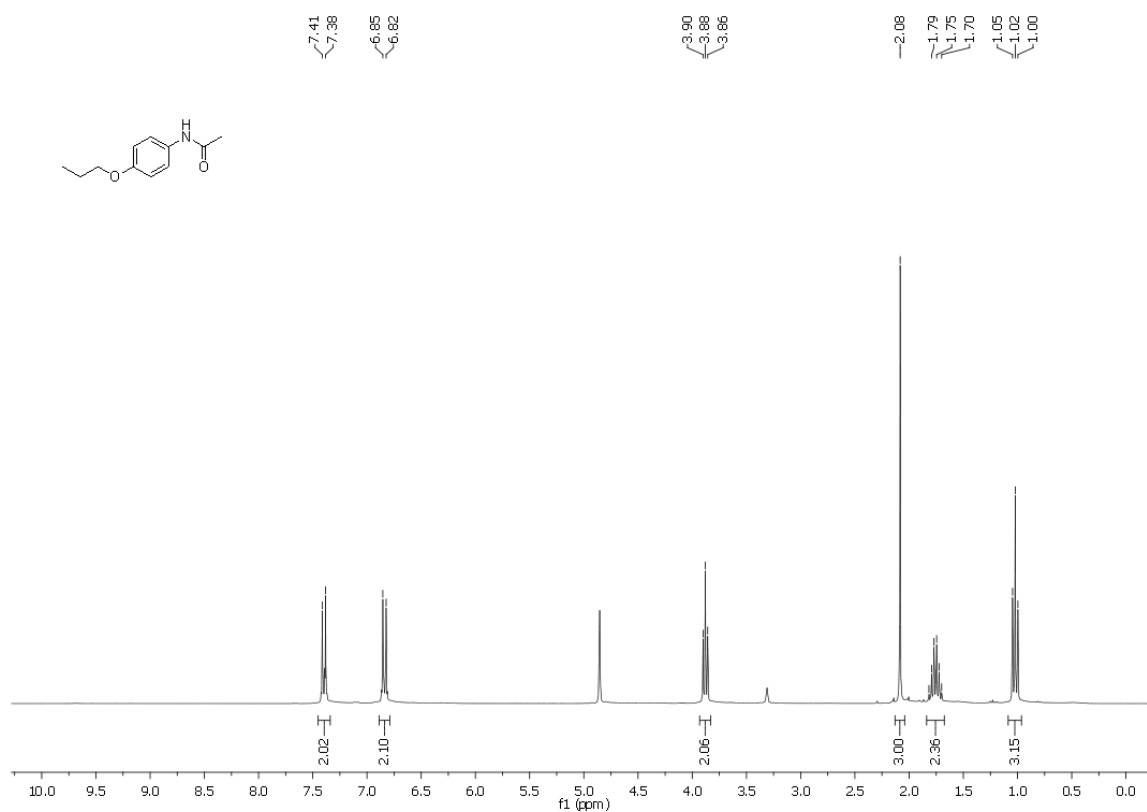
B8 3-nitro-4-propoxyacetanilide (**2h**)



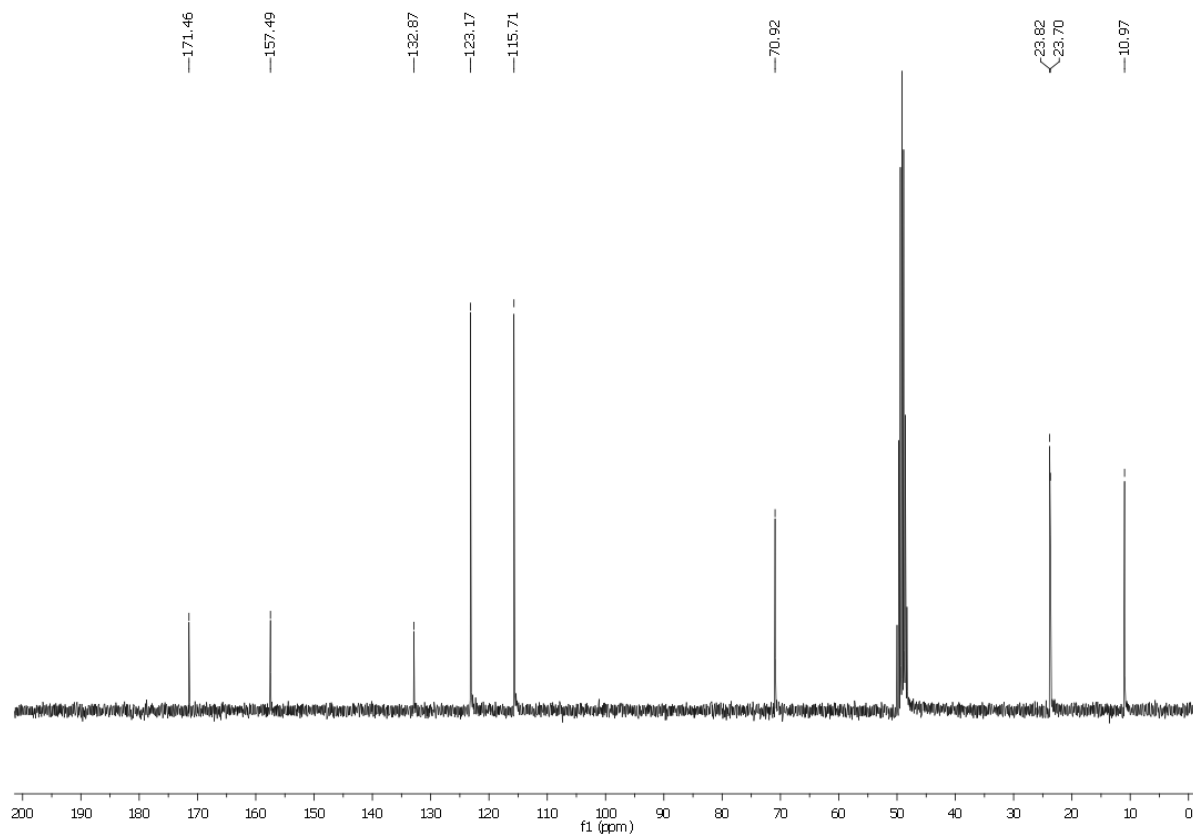
**4-Propoxyacetanilide:** 4-Hydroxyacetanilide (**1**) (13.3 mmol, 2.00 g),  $K_2CO_3$  (29.3 mmol, 4.10 g) and Iodopropane (31.8 mmol, 5.40 g, 3.1 mL) in acetone (30 mL) were heated to reflux for 24 hours. The solution was concentrated in vacuum and the residue dissolved with EtOAc and water. The aqueous layer was extracted three times with EtOAc (30 mL each). The combined organic layers were dried with  $MgSO_4$  and concentrated in vacuum. The residue was purified by column chromatography ( $SiO_2$ , EtOAc:MTBE 1:3) to give 4-propoxyacetanilide as a pale solid in 93 % (12.4 mmol, 2.39 g) yield, mp  $123^\circ C$  (reported in the literature:<sup>8</sup>  $118-122^\circ C$ ).  $^1H$  NMR (300 MHz,  $CD_3OD$ )  $\delta$  7.40 (d,  $J = 9.1$ , 2H), 6.84 (d,  $J = 9.1$ , 2H), 3.88 (t,  $J = 6.5$ , 2H), 2.08 (s, 3H), 1.76 (tq,  $J = 7.4$ , 6.5, 2H), 1.02 (t,  $J = 7.4$ , 3H);  $^{13}C$  NMR (75 MHz,  $CD_3OD$ )  $\delta$  171.5, 157.5, 132.9, 123.2, 115.7, 70.9, 23.8, 23.7, 11.0; IR (KBr-disc)  $\nu$  3253 (m), 3140 (m), 2963 (s), 2874 (s), 1655 (s), 1508 (s); MS (EI)  $m/z = 150$  (4 %), 193 (6 %); HRMS (EI)  $m/z$  calcd for  $C_{11}H_{15}NO_2^+$   $[M]^+$ : 193.1103, found 193.1114; Anal. calcd for  $C_{11}H_{15}NO_2$ : C, 68.4 %; H, 7.8 %; N, 7.3 %; found C, 68.3 %; H, 7.9 %; N, 7.2 %.

<sup>8</sup> O. Hinsberg, *Liebigs Ann.*, 1899, **305**, 276-289

### $^1\text{H}$ NMR (300 MHz, $\text{CD}_3\text{OD}$ )

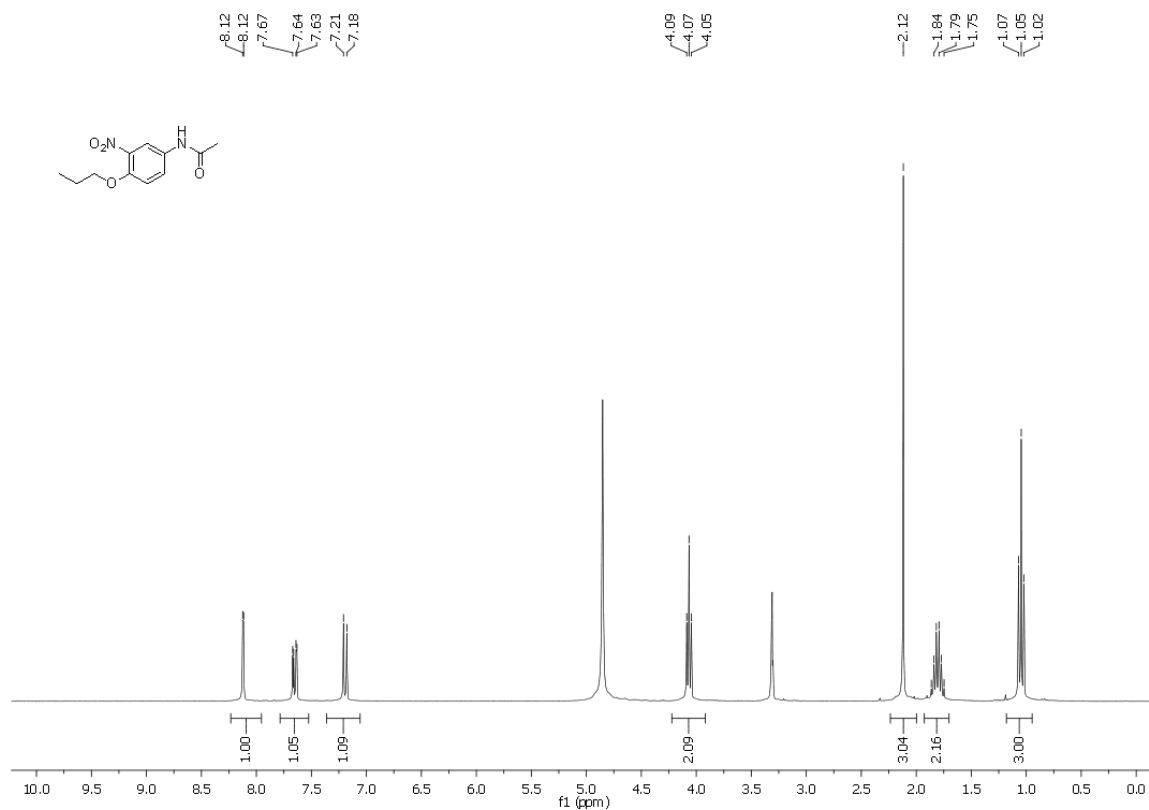


### $^{13}\text{C}$ NMR (75 MHz, $\text{CD}_3\text{OD}$ )

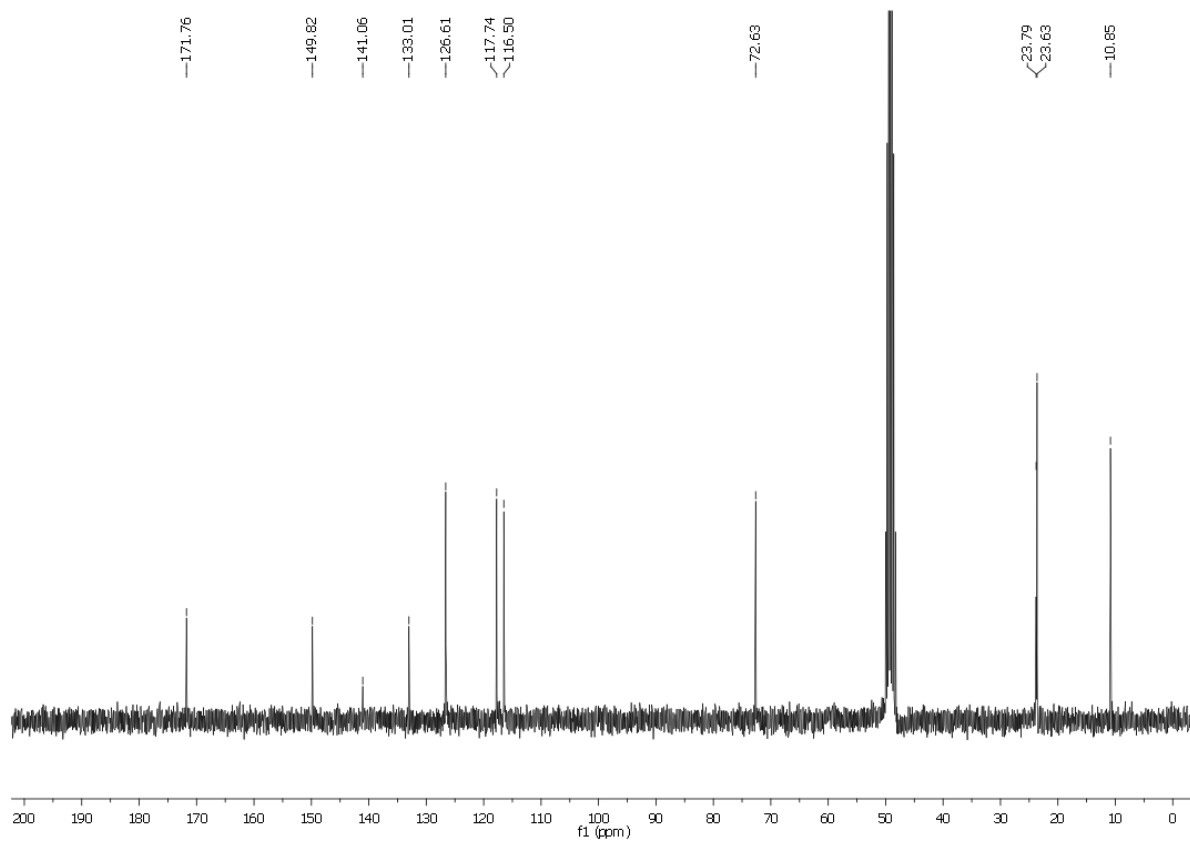


**3-nitro-4-propoxyacetanilide (2h):** 4-Propoxyacetanilide (1.0 mmol, 200 mg) was slowly added to ice-cold sulfuric acid (2.0 mL 85 % solution in water) and stirred until the solid was dissolved. Guanidinium nitrate (1.3 mmol, 152 mg) was added to the reaction mixture over a period of 30 minutes. After stirring for three hours at 0-5°C, ice water (20 mL) was carefully added, and the resulting precipitate was dissolved in EtOAc. The aqueous layer was extracted three times with EtOAc (10 mL each). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuum. The residue was purified by column chromatography (SiO<sub>2</sub>, EtOAc:MTBE 1:3) to give 3-nitro-4-propoxyacetanilide (**2h**) as a yellow solid in 90 % (0.94 mmol, 220 mg) yield, mp 109°C. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ 8.12 (d, *J* = 2.7, 1H), 7.64 (dd, *J* = 2.7, 9.1, 1H), 7.17 (d, *J* = 9.1, 1H), 4.05 (t, *J* = 6.3, 2H), 2.12 (s, 3H), 1.80 (tq, *J* = 7.4, 6.3, 2H), 1.04 (t, *J* = 7.4, 3H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) δ 171.8, 149.8, 141.1, 133.0, 126.6, 117.7, 116.5, 72.6, 23.8, 23.6, 10.8; IR (KBr-disc) ν 3297.5 (m), 3120 (m), 1666 (s), 1528 (s), 1257 (s); MS (EI) *m/z* 154 (100 %), 196 (29 %), 238 (23 %); HRMS (EI) *m/z* calcd for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup> [M]<sup>+</sup>: 238.0954, found 238.0966; Anal. calcd for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>: C, 55.5 %; H, 5.9 %; N, 11.8 %; found C, 55.6 %; H, 5.9 %; N, 11.8 %.

### $^1\text{H}$ NMR (300 MHz, $\text{CD}_3\text{OD}$ )

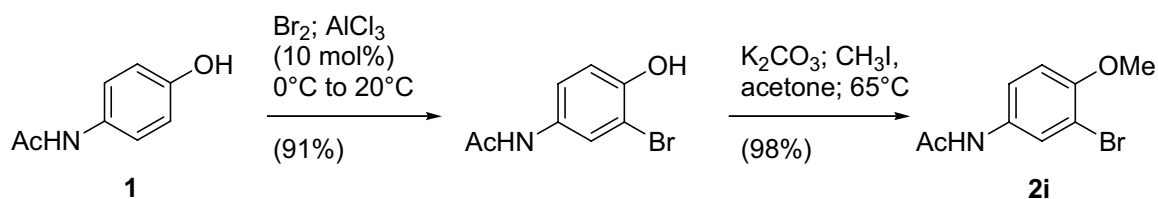


### $^{13}\text{C}$ NMR (75 MHz, $\text{CD}_3\text{OD}$ )





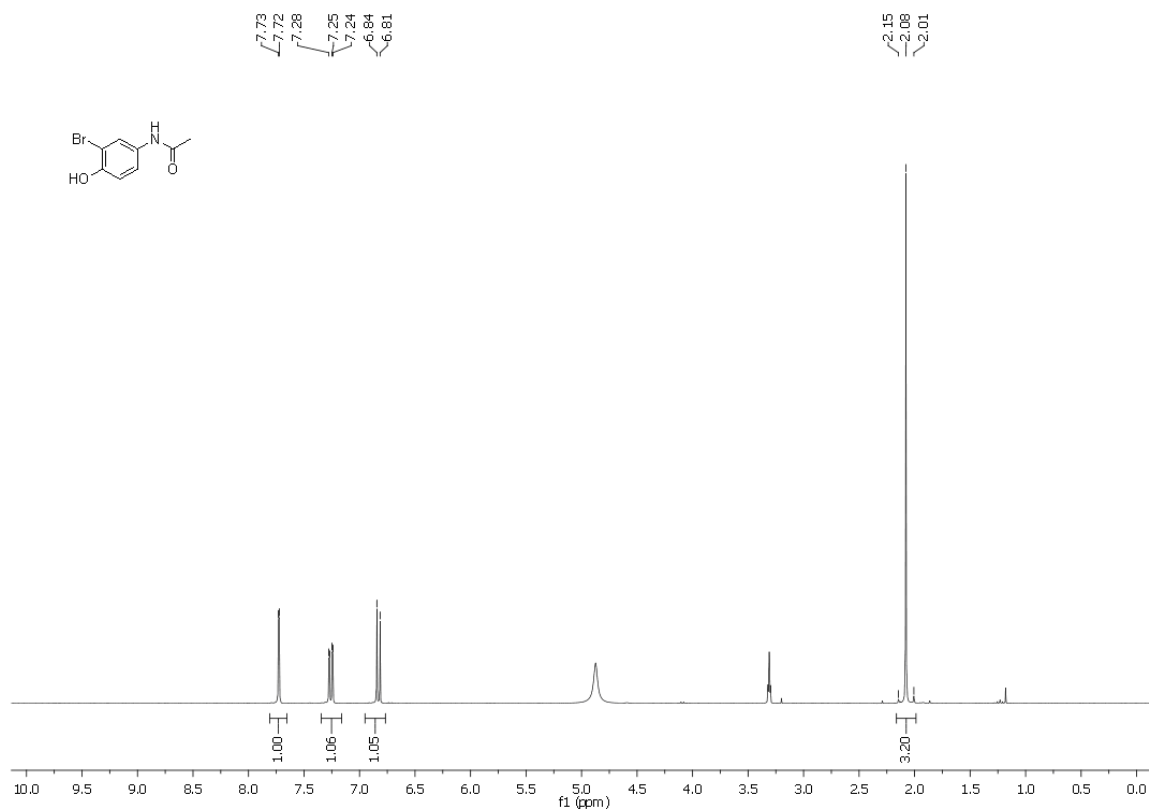
B9 3-Bromo-4-methoxyacetanilide (**2i**)



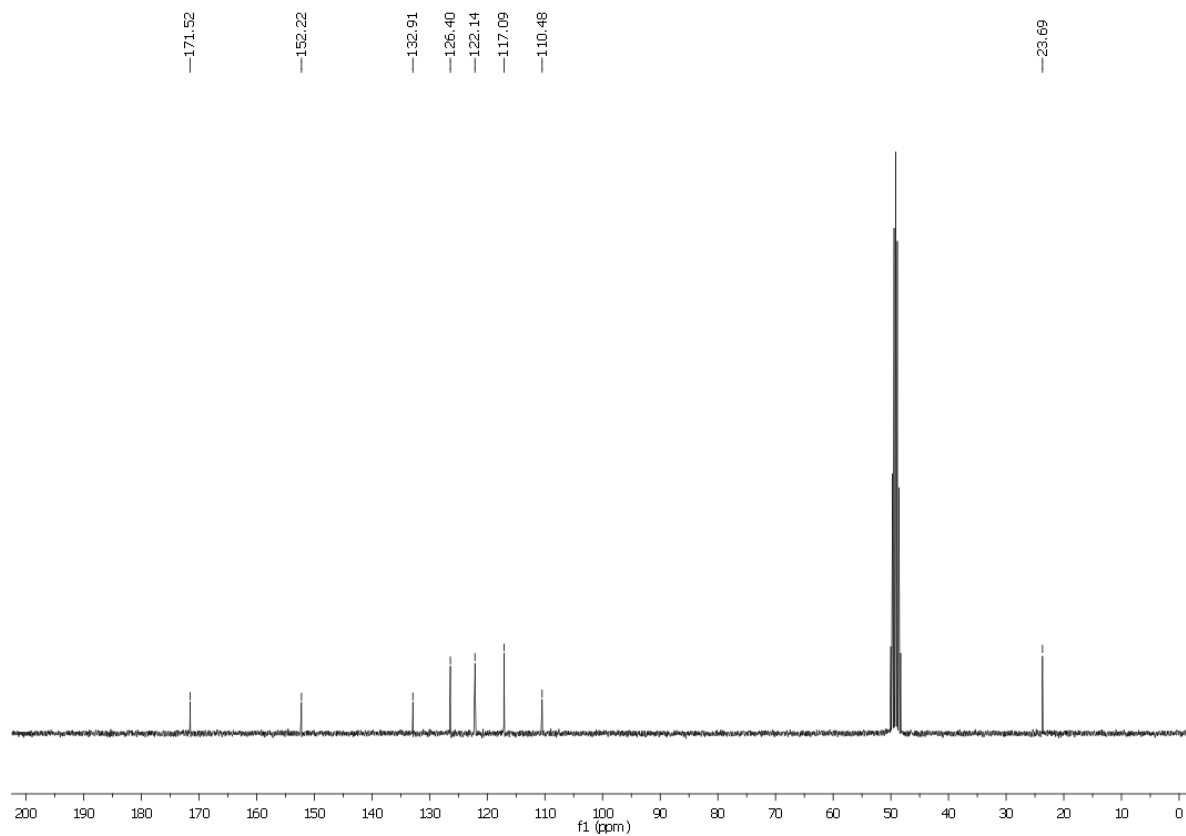
**3-Bromo-4-hydroxyacetanilide:** 4-Hydroxyacetanilide (**1**) (13.2 mmol, 2.00 g) and AlCl<sub>3</sub> (10 mol%, 1.3 mmol, 186 mg) in DCM (40 mL) were cooled to 0°C. A solution of bromine (13.2 mmol, 2.12 g, 0.70 mL) in DCM (10 mL) was then added dropwise over a period of 30 minutes. The resulting suspension was stirred at room temperature for 12 hours, and was then washed with a saturated aqueous solution of sodium thiosulfate (10 mL) until the brownish colour disappeared. The aqueous layer was extracted three times with MTBE (20 mL each). The combined organic layers were dried with MgSO<sub>4</sub> and evaporated in vacuum. The residue was purified by column chromatography (SiO<sub>2</sub>, EtOAc:MTBE 1:3) to give 3-bromo-4-hydroxyacetanilide as a pale solid in 91 % (12.0 mmol, 2.75 g) yield, mp 156°C (reported in the literature:<sup>9</sup> 155-157°C). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ 7.73 (d, *J* = 2.5, 1H), 7.26 (dd, *J* = 2.5, 8.7, 1H), 6.83 (d, *J* = 8.7, 1H), 2.08 (s, 3H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) δ 171.5, 152.2, 132.9, 126.4, 122.1, 117.1, 110.5, 23.7; IR (KBr-disc) ν 3159 (m), 1623 (s), 1547 (s), 1409 (s), 1285 (s); MS (EI) *m/z* 150 (4 %), 187 (100 %), 229 (M<sup>+</sup>, 26 %); HRMS (EI) *m/z* calcd for C<sub>8</sub>H<sub>8</sub>BrNO<sub>2</sub><sup>+</sup> [M]<sup>+</sup>: 228.9738, found 228.9751; Anal. calcd for C<sub>8</sub>H<sub>8</sub>BrNO<sub>2</sub>: C, 41.8 %; H, 3.5 %; N, 6.1 %; found C, 42.0 %; H, 3.6 %; N, 6.1 %.

<sup>9</sup> O. Hodurek, *Ber. Dt. Chem. Ges.*, 1897, **30**, 477-480.

$^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ )



$^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{OD}$ )

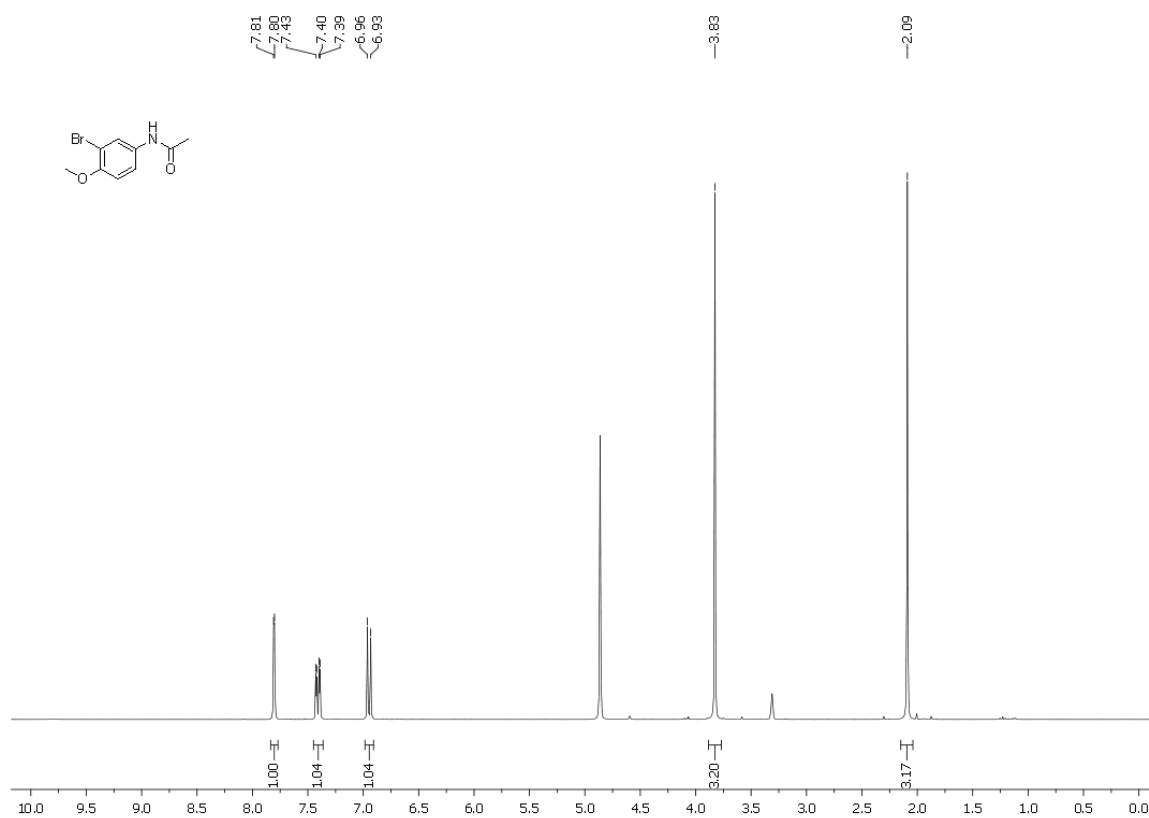


**3-Bromo-4-methoxyacetanilide (2i):**<sup>10</sup> 3-Bromo-4-hydroxyacetanilide (4.4 mmol, 1.00 g), K<sub>2</sub>CO<sub>3</sub> (8.7 mmol, 1.20 g) and iodomethane (8.7 mmol, 1.24 g, 0.55 mL) in dry DMF (20 mL) were heated to 40°C for six hours and stirred at room temperature for 12 hours under nitrogen. The solution was concentrated in vacuum and the residue dissolved with EtOAc and water. The aqueous layer was extracted three times with EtOAc (20 mL each). The combined organic layers were dried with MgSO<sub>4</sub>, filtered and evaporated. The residue was purified by column chromatography (SiO<sub>2</sub>, EtOAc:MTBE 1:3) to give 3-bromo-4-methoxyacetanilide (**2i**) as a pale solid in 98 % (4.27 mmol, 1.04 g) yield, mp 114°C (reported in the literature:<sup>11</sup> 115°C). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ 7.81 (d, *J* = 2.5, 1H), 7.41 (dd, *J* = 2.5, 8.9, 1H) 6.95 (d, *J* = 8.9, 1H), 3.83 (s, 3H), 2.09 (s, 3H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) δ 171.6, 154.2, 134.0, 126.5, 121.7, 113.3, 112.2, 57.0, 23.8; IR (KBr-disc) ν 3235 (m), 1657 (s), 1497 (s), 1440 (s); LRMS (ESI) *m/z* 244 (60%), 219 (14 %), 165 (100 %), 121 (14 %); HRMS (ESI) *m/z* calcd for C<sub>9</sub>H<sub>11</sub>BrNO<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 243.9973, found 243.9957; Anal. calcd for C<sub>9</sub>H<sub>10</sub>BrNO<sub>2</sub>: C, 44.3 %; H, 4.1 %; N, 5.7 %; found C, 44.3 %; H, 3.7 %; N, 5.7 %.

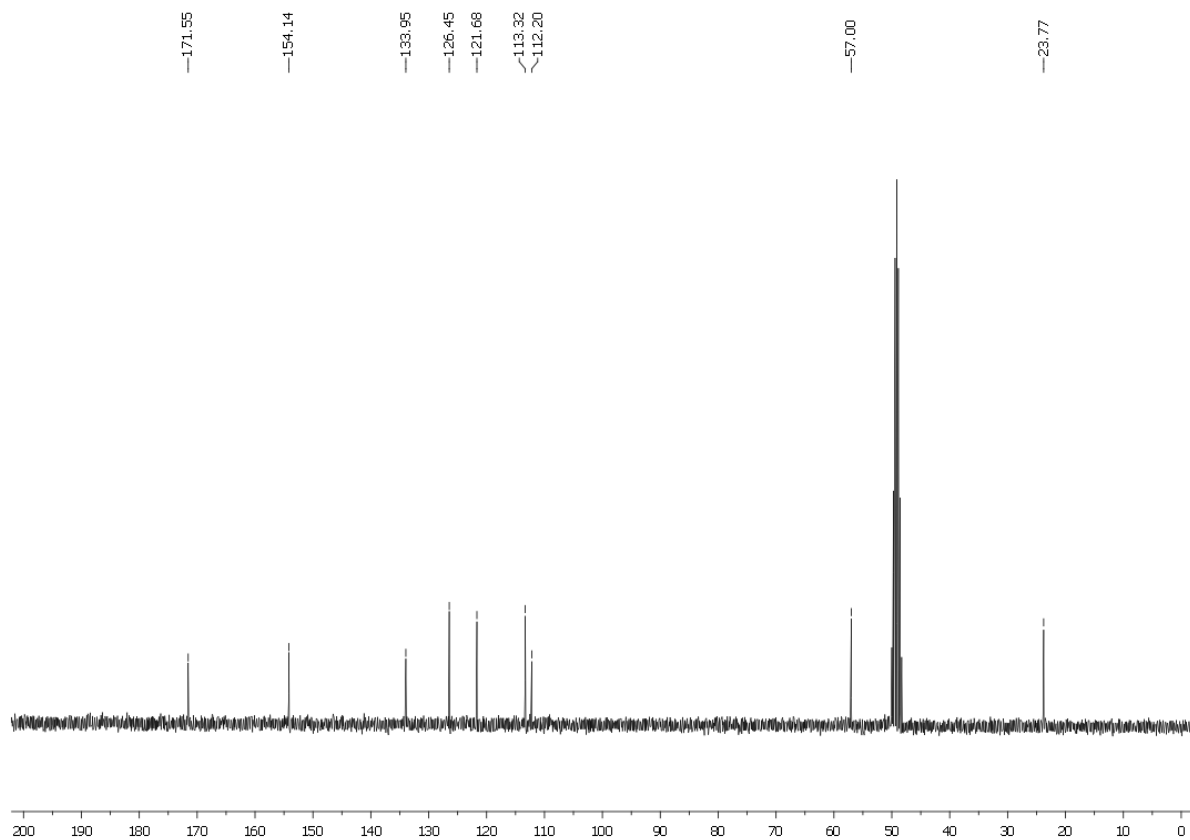
<sup>10</sup>P. M. O'Neill, D. J. Willock, S. R. Hawley, P. G. Bray, R. C. Storr, S. A. Ward and B. K. Park, *J. Med. Chem.*, 1997, **40**, 437-448.

<sup>11</sup>H. Mitchell and Y. Leblanc, *J. Org. Chem.*, 2002, **59**, 682-687.

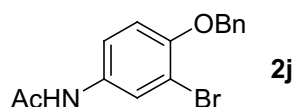
$^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ )



$^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{OD}$ )

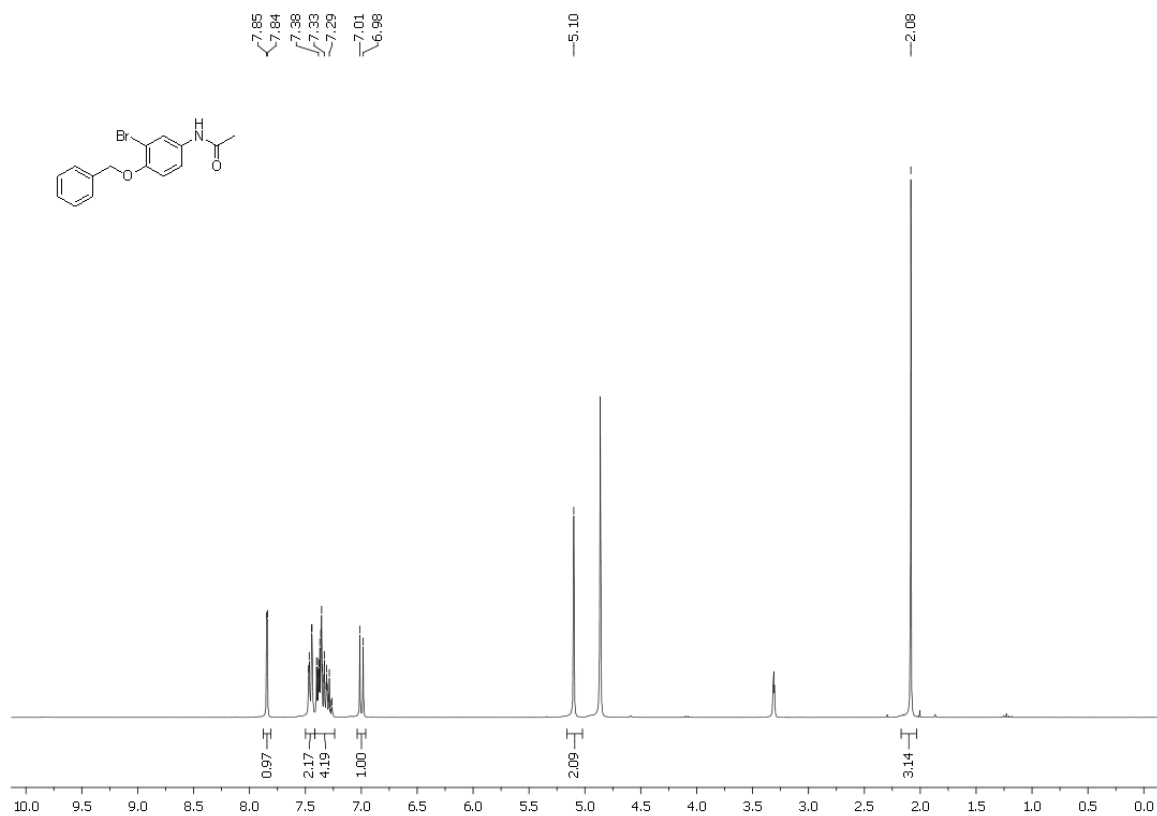


B10 4-Benzoyloxy-3-bromoacetanilide (**2j**)

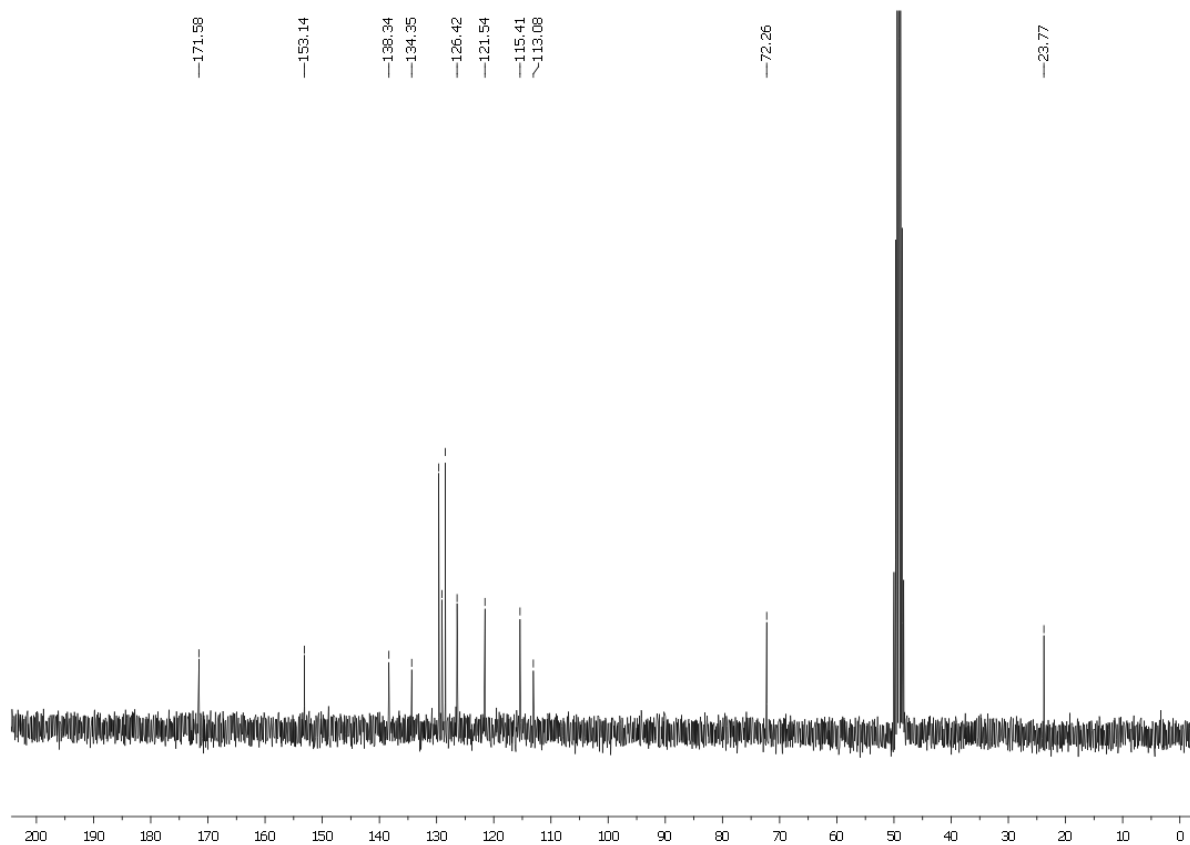


3-Bromo-4-hydroxyacetanilide (4.4 mmol, 1.00 g), synthesized as described in section B9,  $K_2CO_3$  (5.2 mmol, 0.72 g) and benzyl bromide (5.2 mmol, 0.90 g, 0.63 mL) in acetone (100 mL) were heated to reflux for six hours and then stirred at room temperature for 12 hours. The solution was concentrated in vacuum and the residue was dissolved in EtOAc and water. The aqueous layer was extracted three times with EtOAc (30 mL each). The combined organic layers were dried with  $MgSO_4$  and concentrated in vacuum. The residue was purified by column chromatography ( $SiO_2$ , EtOAc:MTBE 1:2) to give 4-benzoyloxy-3-bromoacetanilide (**2j**) as a pale solid in 98 % (4.27 mmol, 1.36 g) yield, mp 133°C.  $^1H$  NMR (300 MHz,  $CD_3OD$ )  $\delta$  7.84 (d,  $J = 2.5$ , 1H), 7.46 – 7.24 (6H), 7.00 (d,  $J = 8.9$ , 1H), 5.10 (s, 2H), 2.08 (s, 3H);  $^{13}C$  NMR (75 MHz,  $CD_3OD$ )  $\delta$  171.6, 153.2, 138.4, 134.4, 129.6, 129.1, 128.5, 126.4, 121.6, 115.4, 113.1, 72.3, 23.8; IR (KBr-disc)  $\nu$  3317 (s), 1660 (s), 1547 (s), 1494 (s), 1247 (s); MS (ESI)  $m/z$  320 (100 %), 278 (6 %), 150 (4 %), 91 (13 %); HRMS (ESI)  $m/z$  calcd for  $C_{15}H_{15}BrNO_2^+$   $[M+H]^+$ : 320.0286, found 320.0272; Anal. calcd for  $C_{15}H_{14}BrNO_2$ : C, 56.3 %; H, 4.4 %; N, 4.4 %; found C, 56.4 %; H, 4.3 %; N, 4.3 %.

$^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ )



$^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{OD}$ )



## C **Experimental procedures, analytical data and copies of spectra for arene diazonium salts 3**

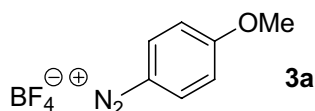
### *C1 General experimental procedure for a one-pot deacetylation/diazotation in aqueous solution*

A suspension of the corresponding acetamide **2** (4.2 mmol) in hydrochloric acid (3M, 15 mL) and methanol (5 mL) was heated to reflux until the solid was completely dissolved (approximately 5 hours). The resulting clear solution was cooled to 0°C, and solid NaNO<sub>2</sub> (0.44 g, 6.3 mmol) was added in small portions. Stirring at this temperature was continued for 1 hour, and NH<sub>4</sub>BF<sub>4</sub> (0.66 g, 6.3 mmol) was then added in small portions. The corresponding diazonium tetrafluoroborate started to precipitate after a few minutes, and stirring at 0°C was further continued for 30 minutes to ensure complete precipitation. The ice-cold suspension was filtered via a Büchner-funnel, and the solid was subsequently washed with cold water (10 mL), ethanol (10 mL), and diethyl ether (50 mL). It was dried in a stream of air to yield the corresponding diazonium tetrafluoroborates **3** as colourless solids.

### *C2 General experimental procedure for a one-pot deacetylation/diazotation in organic reaction media*

To a solution of the corresponding acetanilide **2** (3.0 mmol) in dry methanol (5 mL) was added boron trifluoride-methanol (9.1 mmol, 1.20 g, 0.98 mL). The solution was heated to reflux under an atmosphere of dry nitrogen until the starting acetanilide was completely consumed, as indicated by TLC. The mixture was then cooled to -15°C and *tert*-butyl nitrite (4.5 mmol, 0.47 g, 0.54 mL) was added. Over a period of 15 minutes a colourless precipitate was formed. Stirring was continued for another hour, and the solid was collected by filtration, washed subsequently with cold ethanol (20 mL) and MTBE (20 mL) to give the corresponding diazonium salt **3**.

C3 *para*-Methoxybenzenediazonium tetrafluoroborate (**3a**)

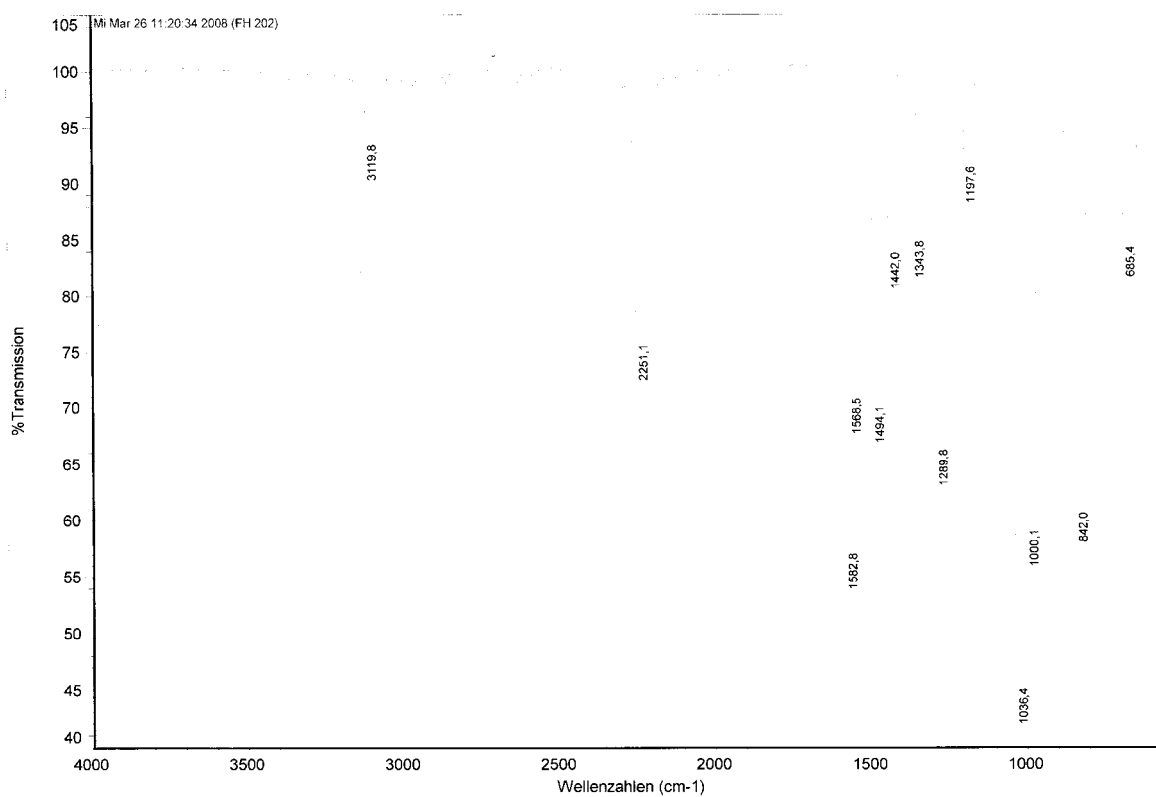


**Procedure C1:** Obtained from **2a** (3.00 g, 18.0 mmol). Yield: 83% (3.30 g, 14.9 mmol).

**Procedure C2:** Obtained from **2a** (500 mg, 3.0 mmol). Yield: 72% (480 mg, 2.2 mmol).

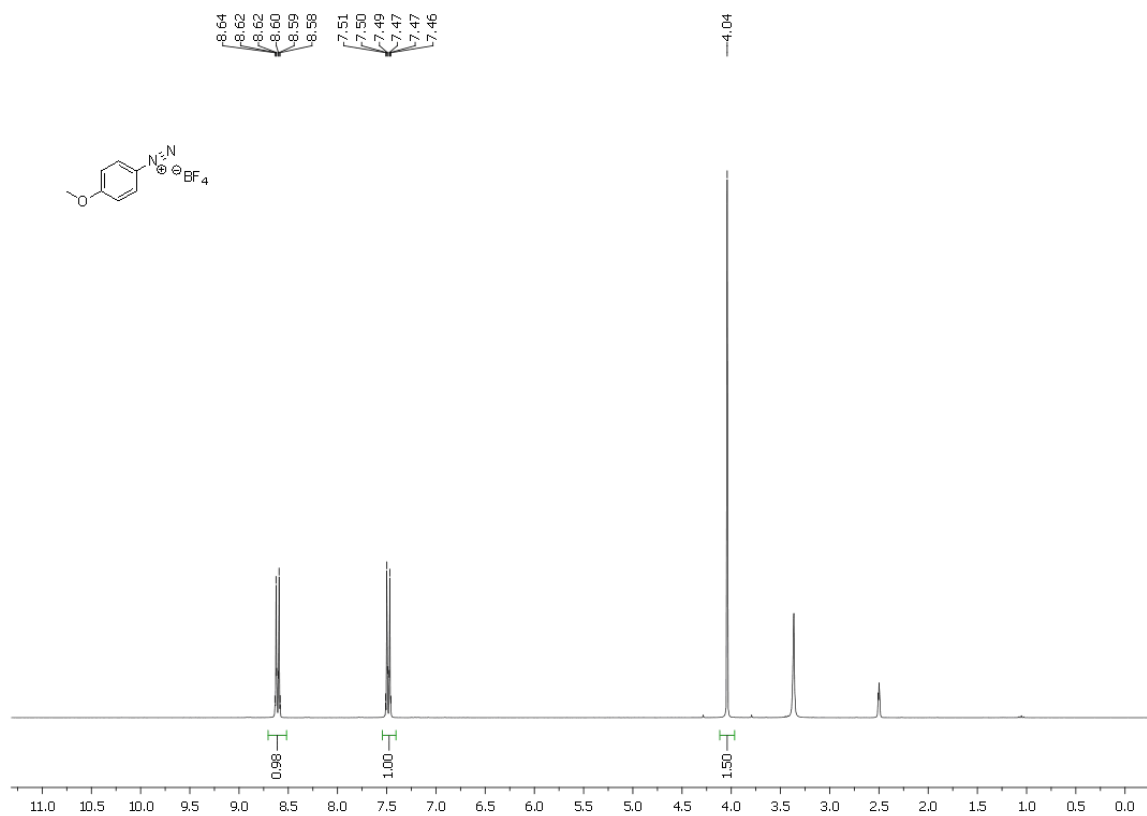
$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.61 (d, 2H,  $J = 9.4$  Hz), 7.48 (d, 2H,  $J = 9.4$  Hz), 4.04 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ , APT)  $\delta$  168.8, 136.1, 117.3, 103.3, 57.4; IR (KBr-disc)  $\nu$  3120 (w), 2251 (m,  $\text{N}_2$ ), 1583 (s), 1569 (s), 1494 (s), 1290 (s), 1036 (s); MS (ESI)  $m/z$  135 (100 %,  $[\text{M}]^+$ ), 107 (51 %), 92 (60 %); HRMS (ESI)  $m/z$  calcd for  $\text{C}_7\text{H}_7\text{N}_2\text{O}^+$   $[\text{M}]^+$ : 135.0553; found 135.0535.

IR (KBr-disc)

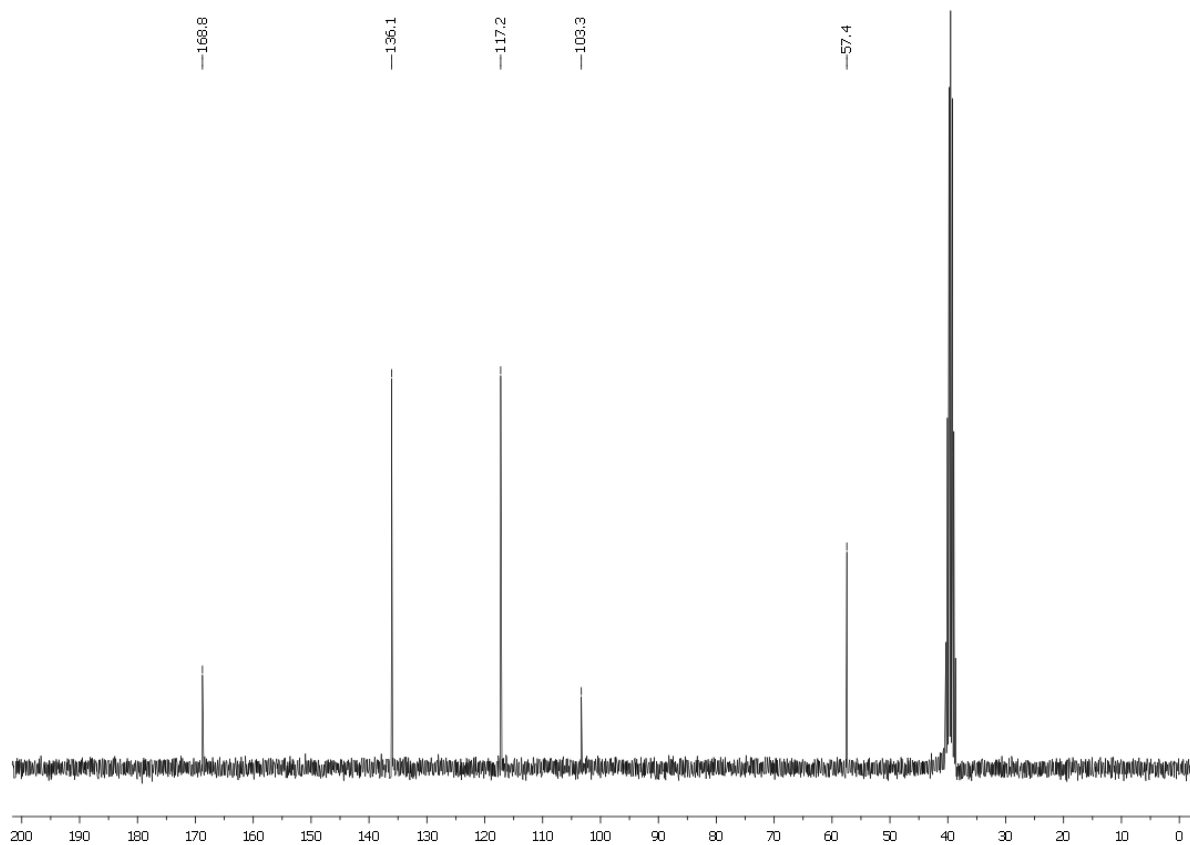




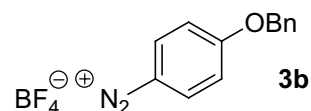
$^1\text{H}$  NMR (300 MHz,  $\text{DMSO-d}_6$ )



$^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO-d}_6$ )



C4 *para*-Benzyloxybenzenediazonium tetrafluoroborate (**3b**)

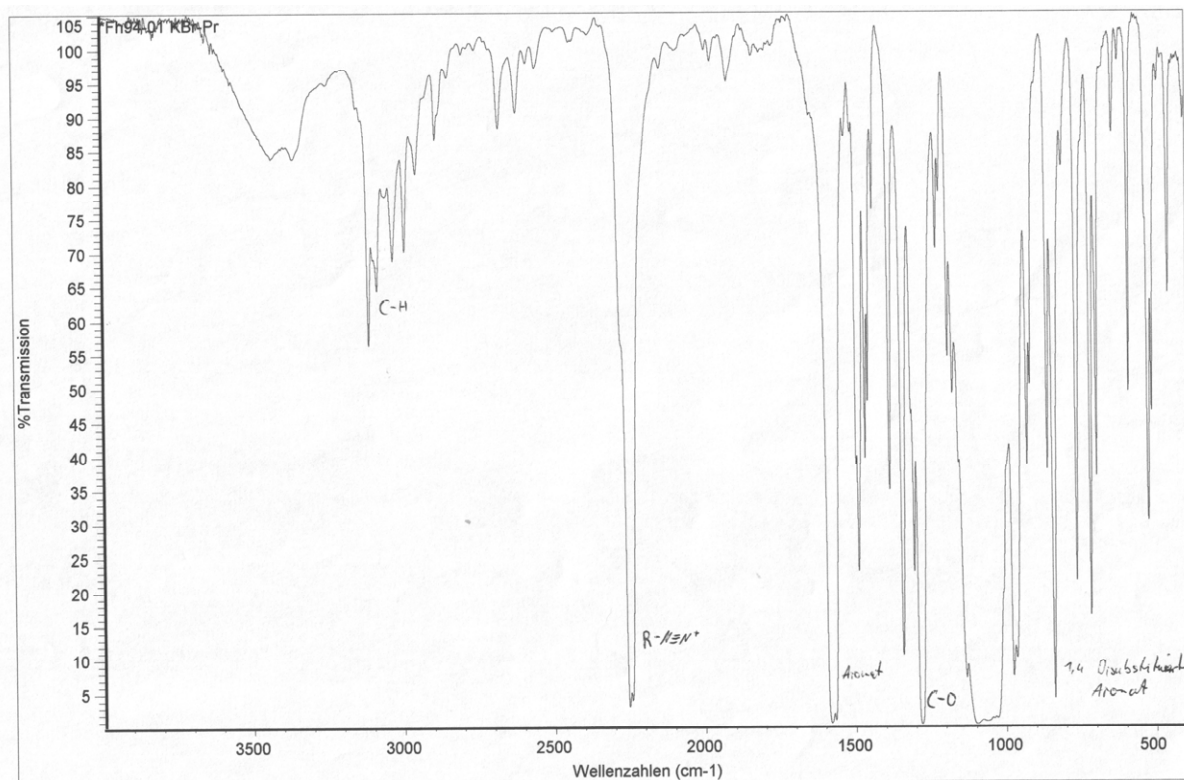


**Procedure C1:** Obtained from **2b** (1.00 g, 4.1 mmol). Yield: 65% (0.81 g, 2.7 mmol).

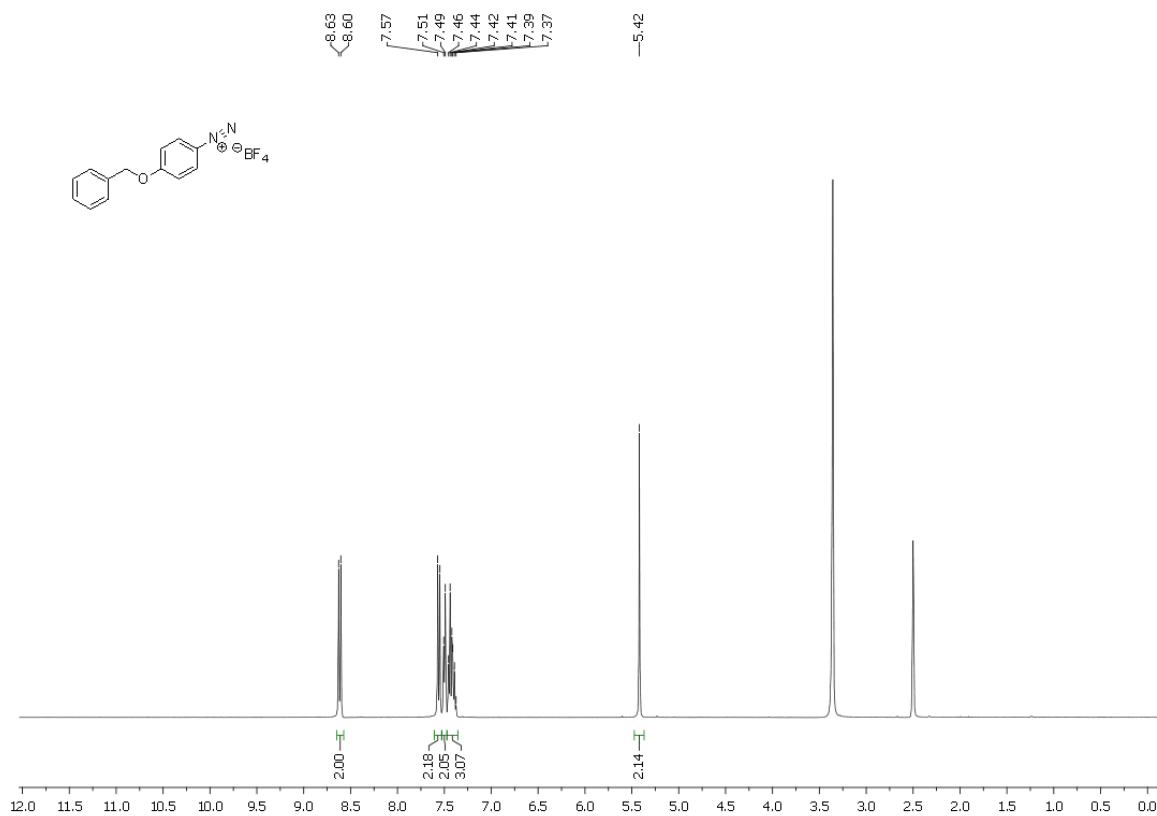
**Procedure C2:** Obtained from **2b** (731 mg, 3.0 mmol). Yield: 71% (690 mg, 2.2 mmol).

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.62 (d, 2H,  $J = 9.4$  Hz), 7.56 (d, 2H,  $J = 9.4$  Hz), 7.51-7.39 (5H), 5.42 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  167.8, 136.2, 134.9, 128.7, 128.7, 128.4, 117.9, 103.7, 71.4; IR (KBr-disc)  $\nu$  3112 (m), 2253 (s,  $\text{N}_2$ ), 1580 (s), 1488 (s), 1280 (s), 1097 (s); MS (FAB+LR)  $m/z$  212 (95 %,  $[\text{M}]^+$ ), 184 (30 %); HRMS (FAB)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}^+$   $[\text{M}]^+$ : 211.0866; found 211.0888; Anal. calcd for  $\text{C}_{13}\text{H}_{11}\text{BF}_4\text{N}_2\text{O}$ : C, 52.4 %; H, 3.7 %; N, 9.4 %; found: C, 52.7 %; H, 3.6 %; N, 9.6 %.

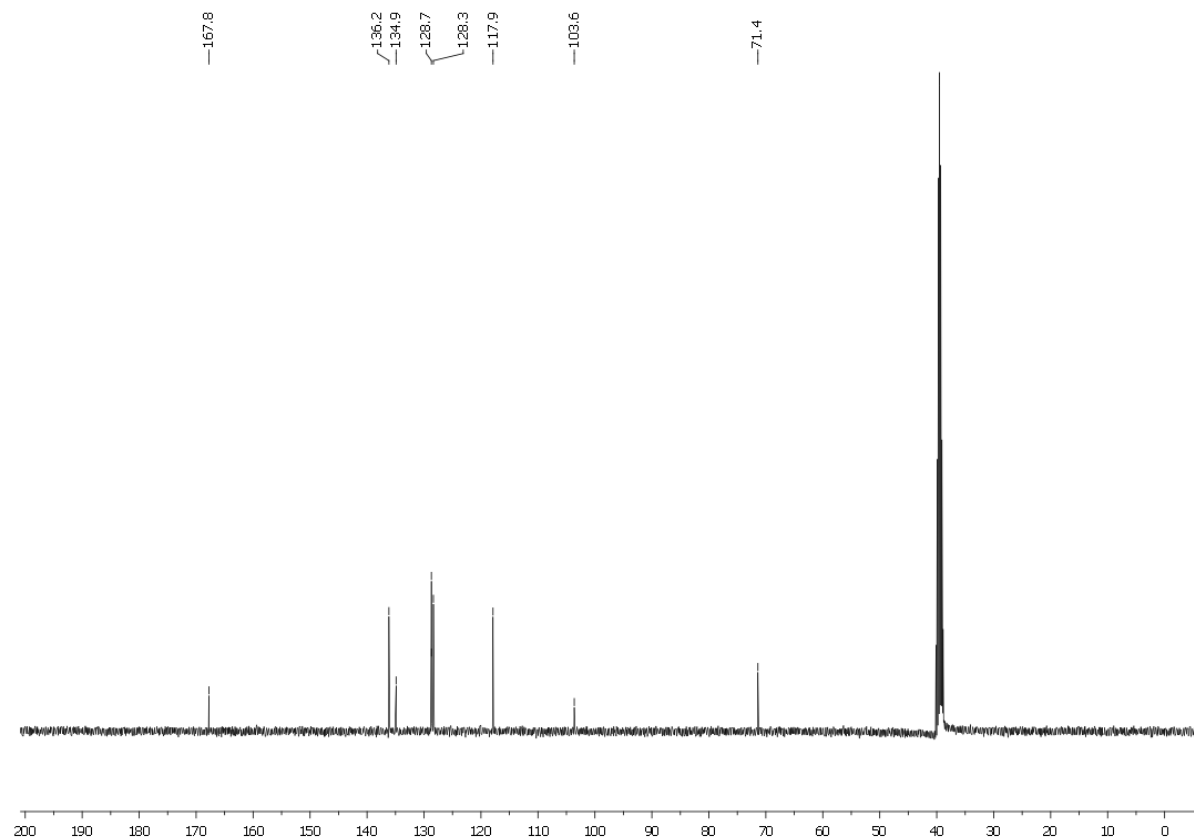
IR (KBr-disc)



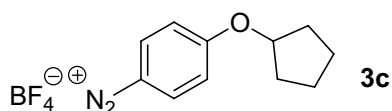
$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )



$^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )



C5 *para*-Cyclopentyloxybenzenediazonium tetrafluoroborate (**3c**)

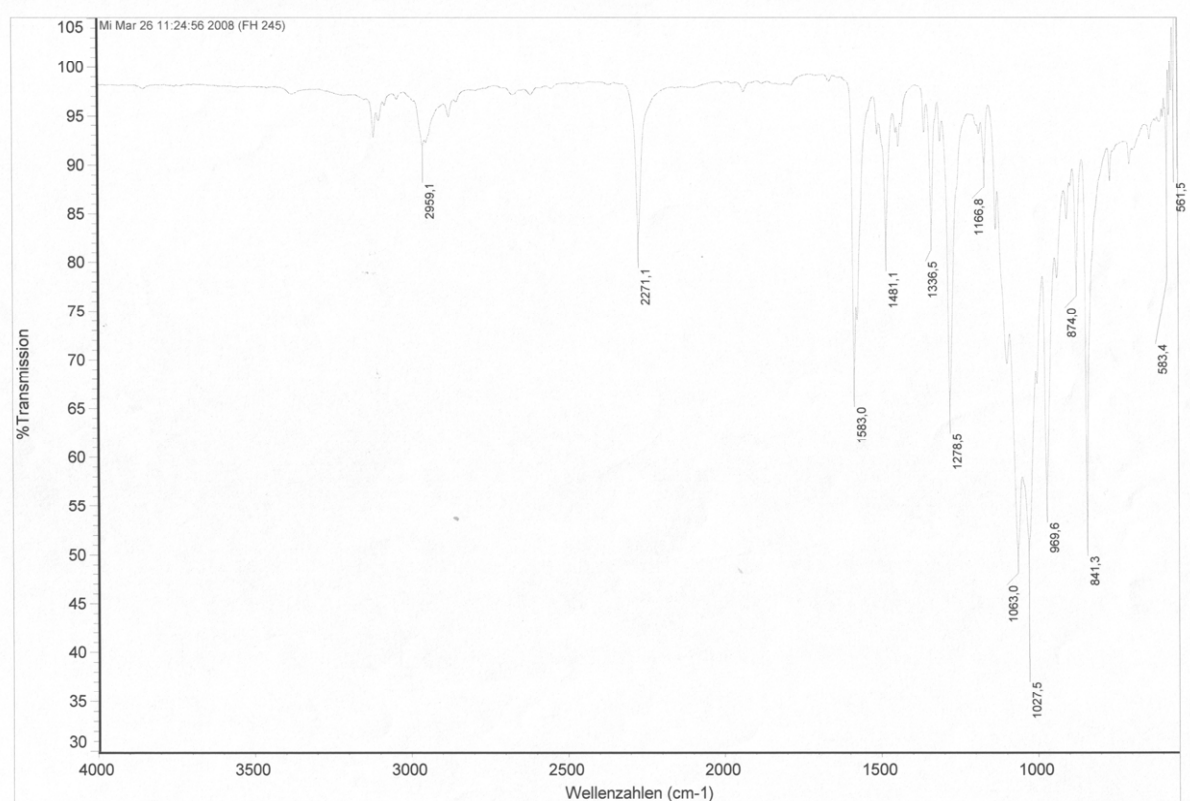


**Procedure C1:** Obtained from **2c** (1.80 g, 8.2 mmol). Yield: 42% (1.00 g, 3.6 mmol).

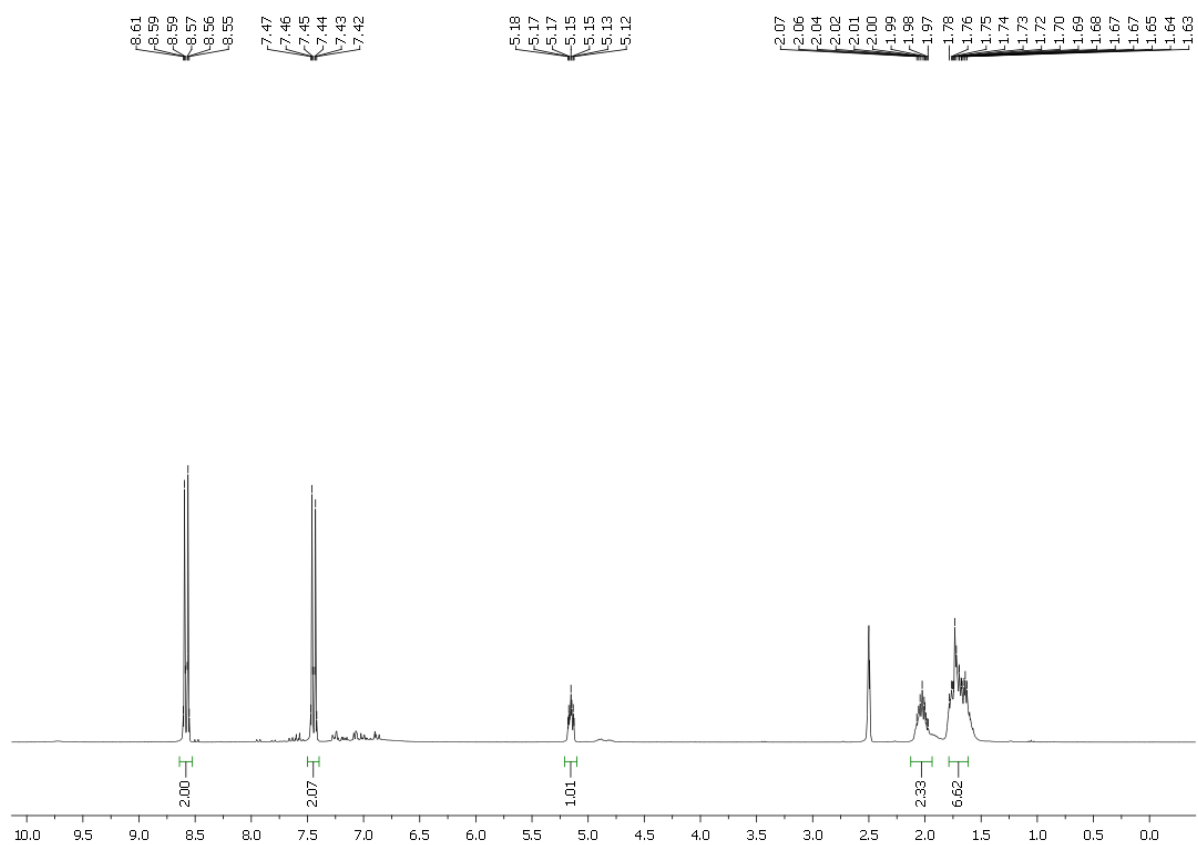
**Procedure C2:** **3c** was not accessible using this protocol.

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.72 (d,  $J = 9.3$ , 2H), 7.49 (d,  $J = 9.3$ , 2H), 5.15 (m, 1H), 2.13 – 1.94 (2H), 1.79 – 1.62 (6H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  167.4, 131.6, 118.2, 102.6, 82.2, 32.2, 23.6; IR (KBr-disc)  $\nu$  2959 (w), 2271 (m,  $\text{N}_2$ ), 1583 (s), 1481 (m) 1337 (m), 1279 (s), 1063 (s), 1028 (s); MS (ESI)  $m/z$  189 (100 %,  $[\text{M}]^+$ ), 190 (20 %); HRMS (ESI):  $m/z$  für  $\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}^+ [\text{M}]^+$ : 189.1022; gefunden: 189.1028.

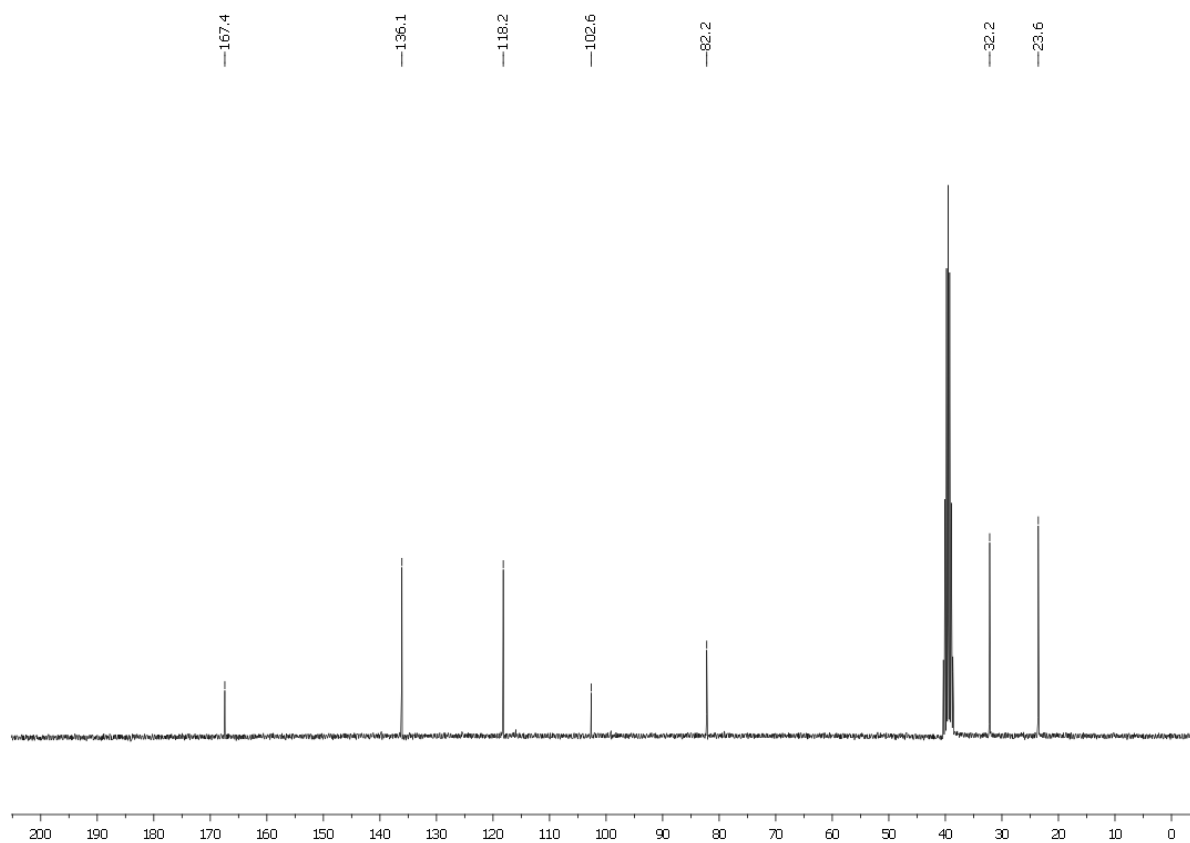
IR (KBr-disc)



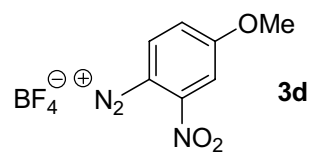
$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )



$^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )



C6 4-Methoxy-2-nitrobenzenediazonium tetrafluoroborate (**3d**)

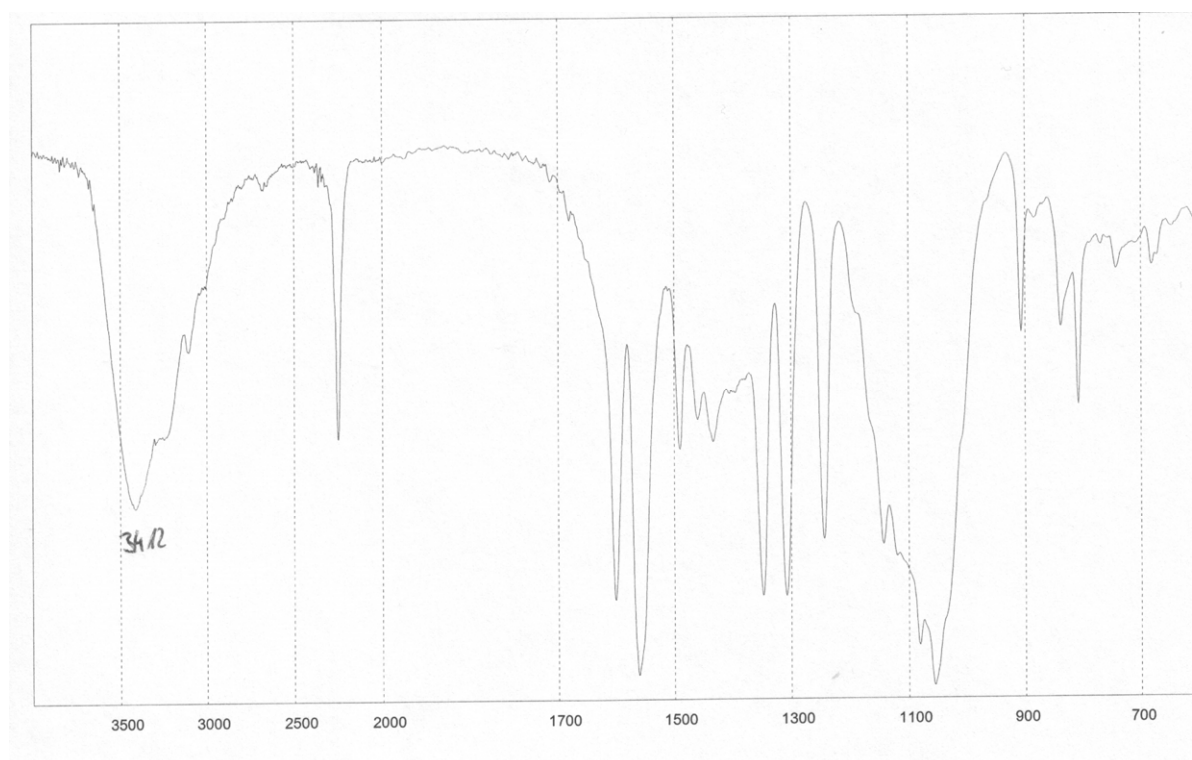


**Procedure C1:** **3d** was not accessible using this protocol.

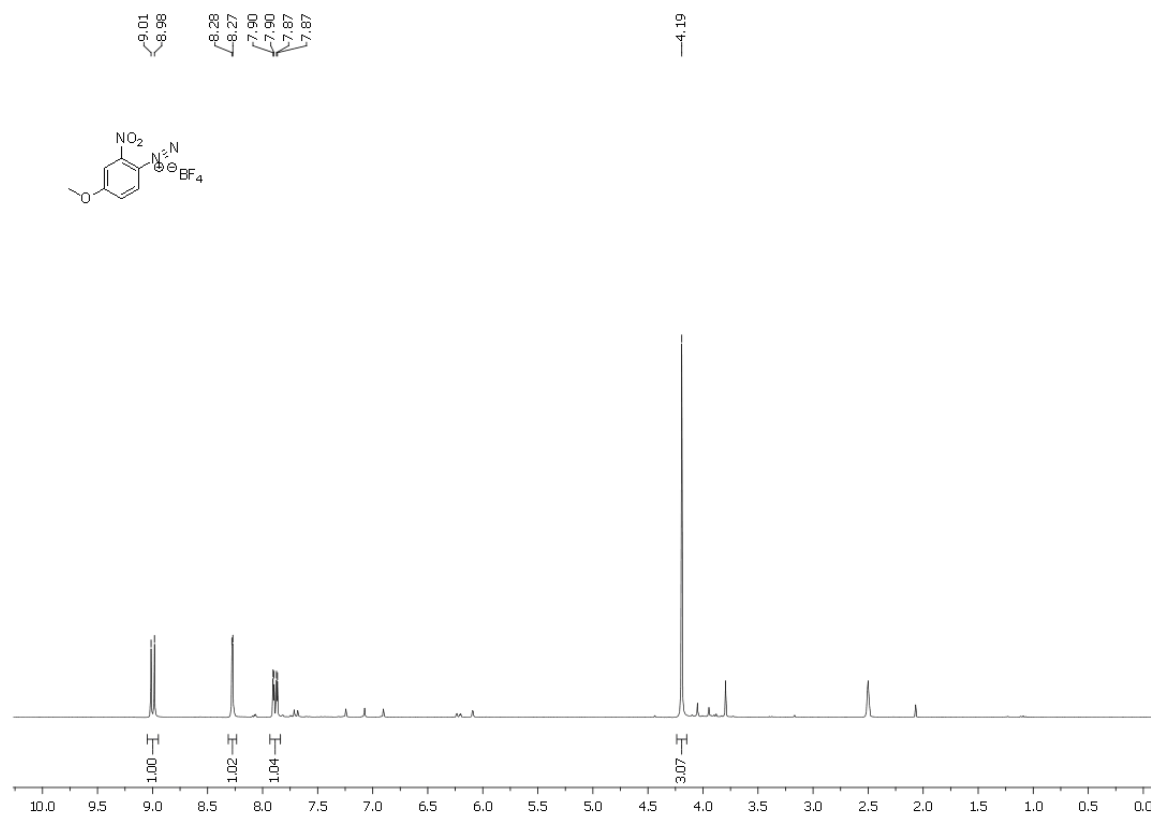
**Procedure C2:** Obtained from **2d** (636 mg, 3.0 mmol). Yield: 92% (742 mg, 2.8 mmol).

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  9.00 (d,  $J = 9.3$ , 1H), 8.27 (d,  $J = 2.5$ , 1H), 7.89 (dd,  $J = 2.6, 9.3$ , 1H), 4.19 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  169.4, 147.6, 139.2, 120.3, 115.8, 98.7, 58.9; IR (KBr-disc)  $\nu$  3412 (m), 2249 (s,  $\text{N}_2$ ), 1601 (s), 1561 (s), 1348 (s); MS (ESI)  $m/z$  180 (100%), 123 (57%), 91 (57%); HRMS (ESI)  $m/z$  calcd for  $\text{C}_7\text{H}_6\text{N}_3\text{O}_3^+$   $[\text{M}]^+$ : 180.0409, found 180.0427.

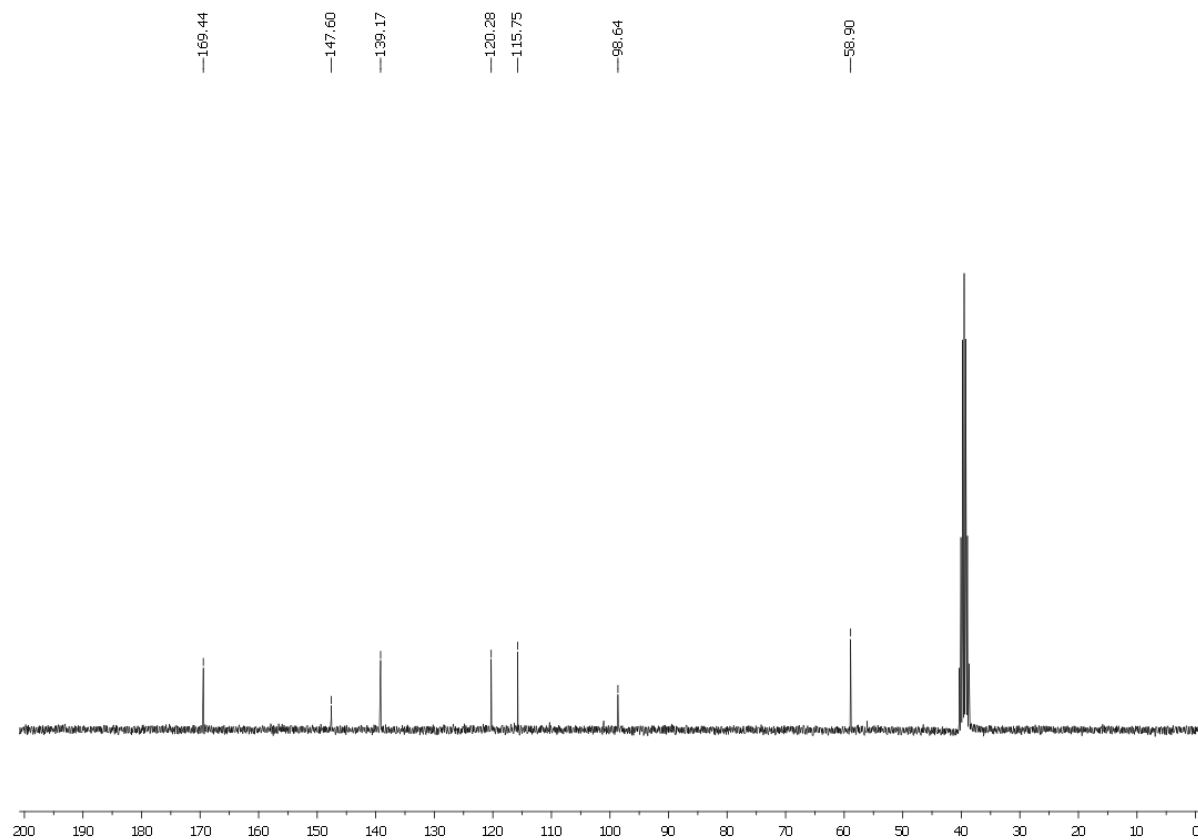
IR (KBr-disc)



$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )



$^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )



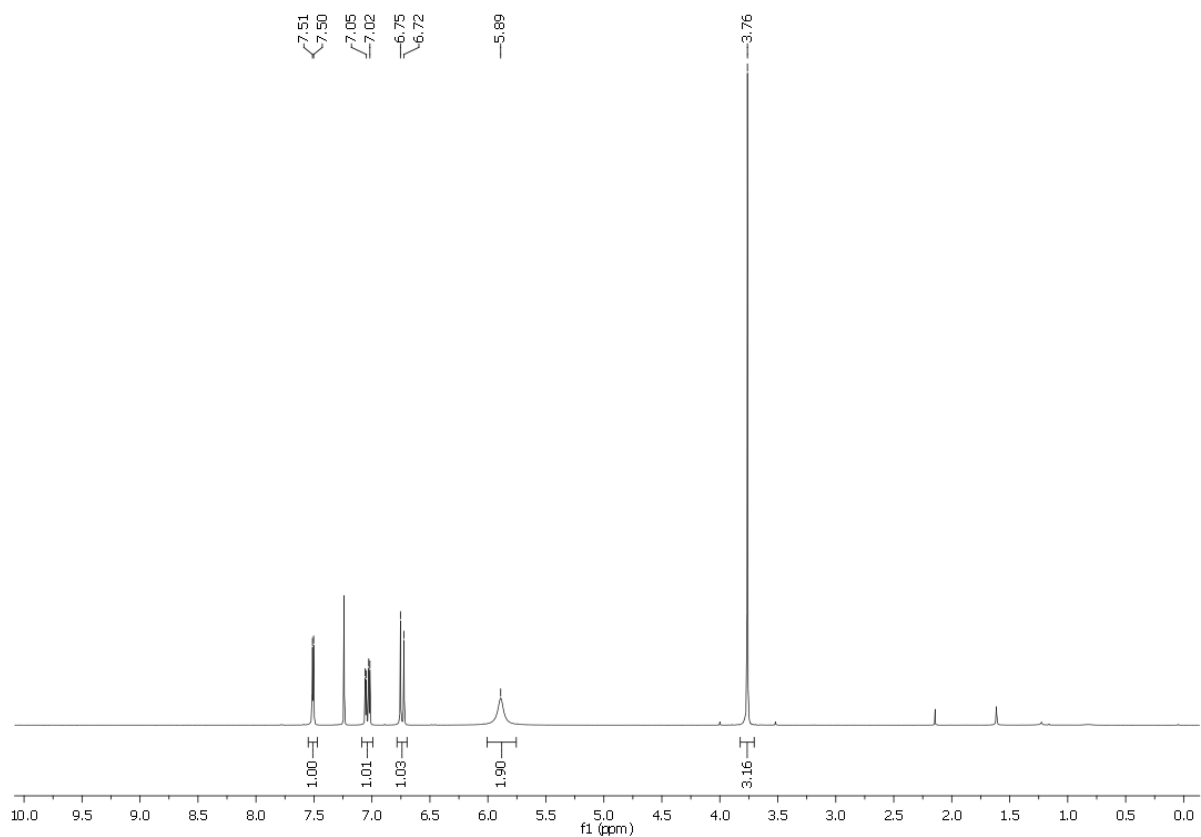
**Two-step procedure for the synthesis of 3d: 4-Methoxy-2-nitroaniline (4d).** A suspension of **2d** (2.4 mmol, 500 mg) in hydrochloric acid (37 %, 1.5 mL) and ethanol (3 mL) was heated to reflux for six hours. To the cold solution was added a concentrated aqueous solution of ammonia (1.2 mL). The solid was filtered off, washed with cold water and dried under vacuum to give 4-methoxy-2-nitroaniline (**4d**) as a red solid in 98 % (2.3 mmol, 392 mg) yield mp 124°C (reported in the literature:<sup>12</sup> 122-130°C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.51 (d, *J* = 3.0, 1H), 7.04 (dd, *J* = 3.0, 9.1, 1H), 6.74 (d, *J* = 9.1, 1H), 5.84 (s(br.), 2H), 3.77 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 151.0, 140.2, 131.7, 126.9, 120.3, 106.5, 56.1; IR (KBr-disc) ν 3487 (m), 3370 (m), 1572 (s), 1501 (w), 1337 (s); MS (EI) *m/z* 122 (35 %), 153 (36 %), 168 (100 %); HRMS (EI) *m/z* calcd for C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> [M]<sup>+</sup>: 168.0535, found 168.0541; Anal. calcd for C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>: C, 50.0 %; H, 4.8 %; N, 16.7 %; found C, 49.4 %; H, 4.9 %; N, 16.7 %.

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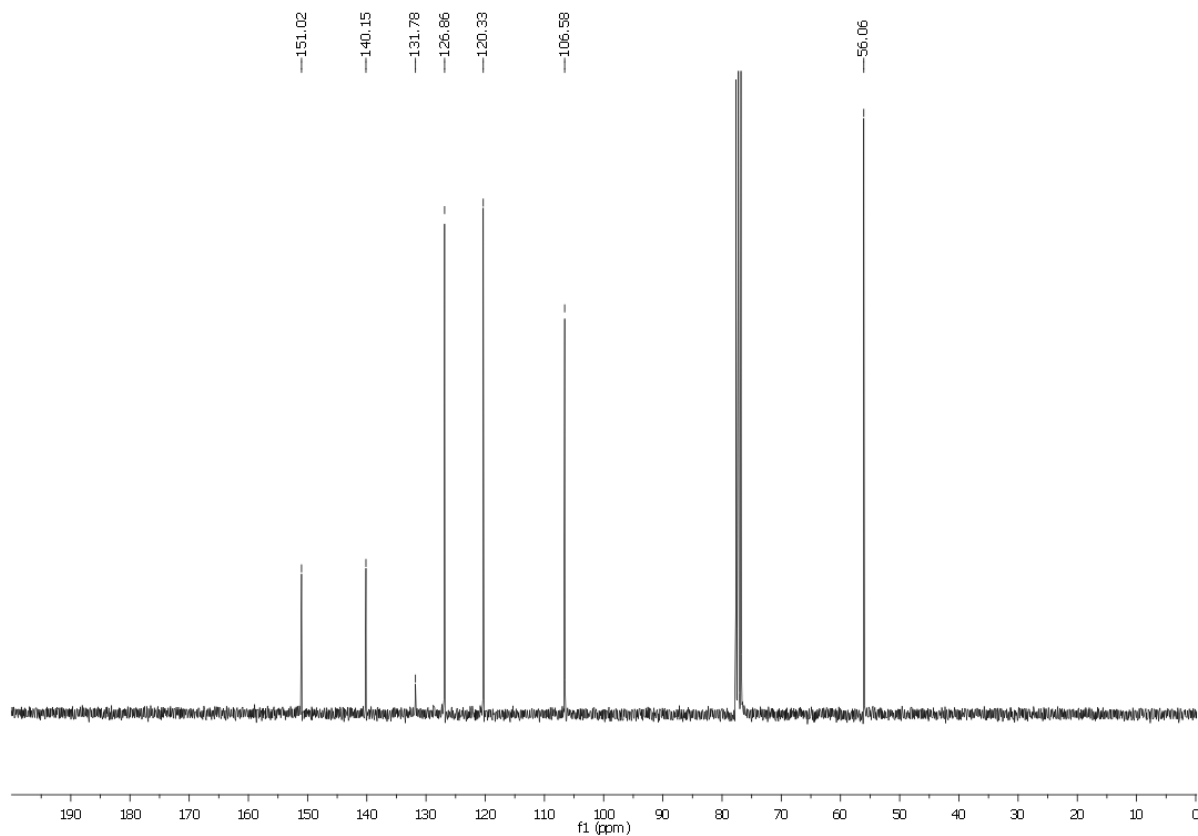
<sup>12</sup> B. Riegel, G. R. Lappin, B. H. Adelson, R. I. Jackson, C. J. Albisetti, R. M. Dodson and R. H. Baker, *J. Am. Chem. Soc.*, 1946, **68**, 1264-1266.



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of **4d**

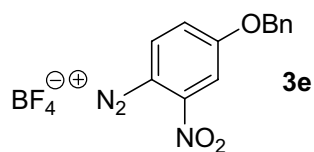


$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) of **4d**



**Synthesis of 4-Methoxy-2-nitrobenzenediazonium tetrafluoroborate (3d) from 4d:** A solution of **4d** (3.2 mmol, 500 mg) in diethylether/acetonitrile (2:1, 10 mL) was cooled to  $-15^{\circ}\text{C}$ .  $\text{BF}_3 \cdot \text{OEt}_2$  (4.8 mmol, 0.61 mL) was added, and the mixture was stirred for 15 minutes. A solution of *tert*-butyl nitrite (3.8 mmol, 0.46 mL) in diethylether (5 mL) was added to the reaction mixture over a period of 10 minutes. Stirring at  $-15^{\circ}\text{C}$  was continued for one hour. The resulting suspension was filtered, and the precipitate was washed with cold ethanol and cold MTBE to give 4-methoxy-2-nitrobenzenediazonium tetrafluoroborate (**3d**) as a pale solid in 83 % (2.7 mmol, 712 mg) yield. All analytical data are identical to those reported above for compound **3d** obtained via Procedure C2.

C7 4-Benzyloxy-2-nitrobenzenediazonium tetrafluoroborate (**3e**)

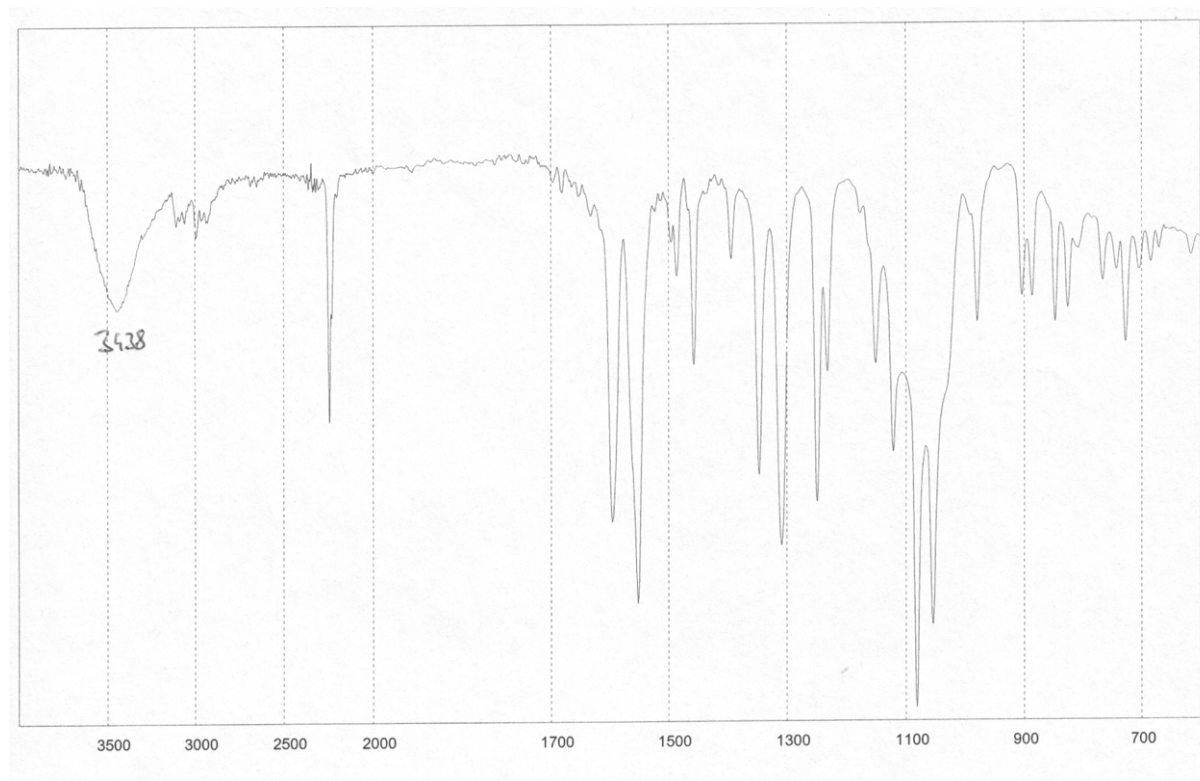


**Procedure C1:** **3e** was not accessible using this protocol.

**Procedure C2:** Obtained from **2d** (867 mg, 3.0 mmol). Yield: 82% (850 mg, 2.5 mmol).

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  9.00 (d,  $J = 9.2$ , 1H), 8.38 (d,  $J = 2.5$ , 1H), 7.97 (dd,  $J = 2.5, 9.3$ , 1H), 7.58 – 7.36 (5H), 5.59 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  168.4, 147.6, 139.1, 134.3, 128.8, 128.7, 128.5, 120.7, 116.4, 98.9, 72.9; IR (KBr-disc)  $\nu$  3438 (m), 2242 (s,  $\text{N}_2$ ), 1596 (s), 1552 (s), 1309 (s); MS (ESI)  $m/z$  256 (56 %), 241 (18 %), 91 (100 %). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{10}\text{N}_3\text{O}_3^+ [\text{M}]^+$ : 256.0722, found 256.0701.

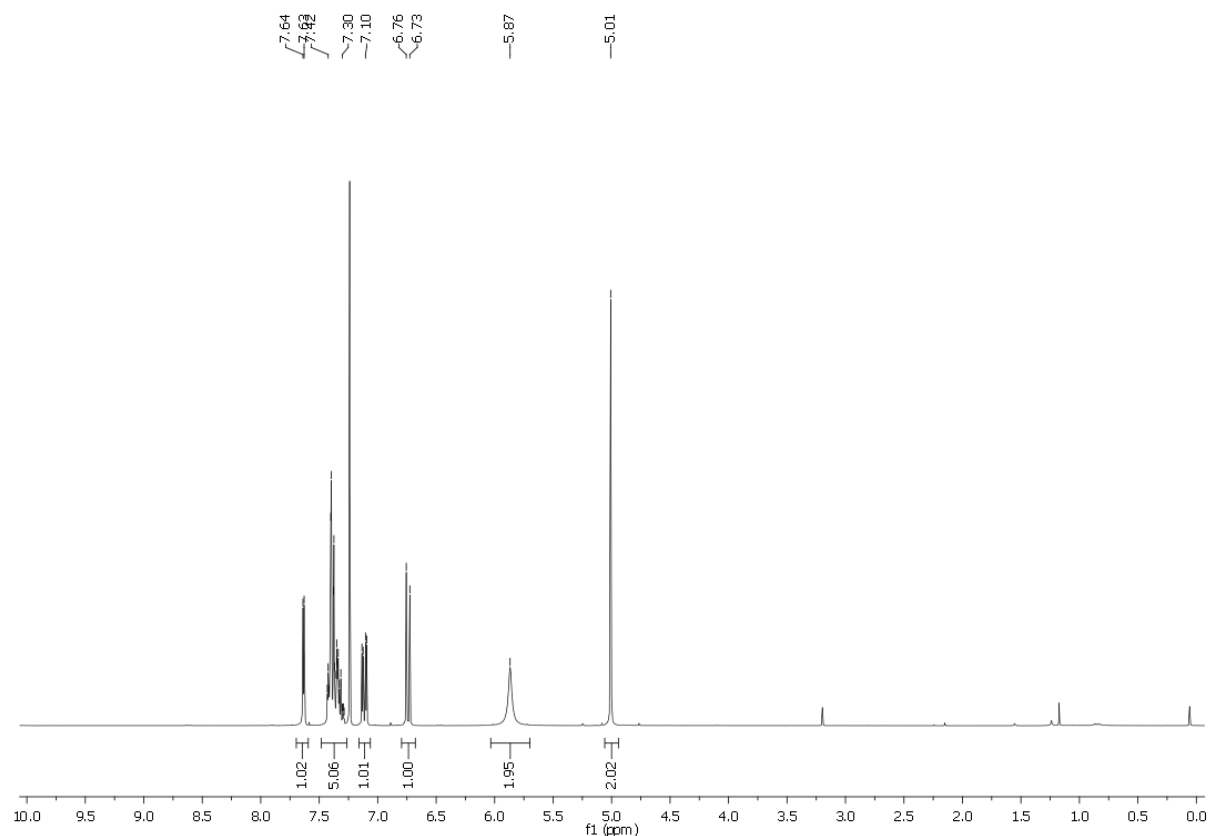
IR (KBr-disc)





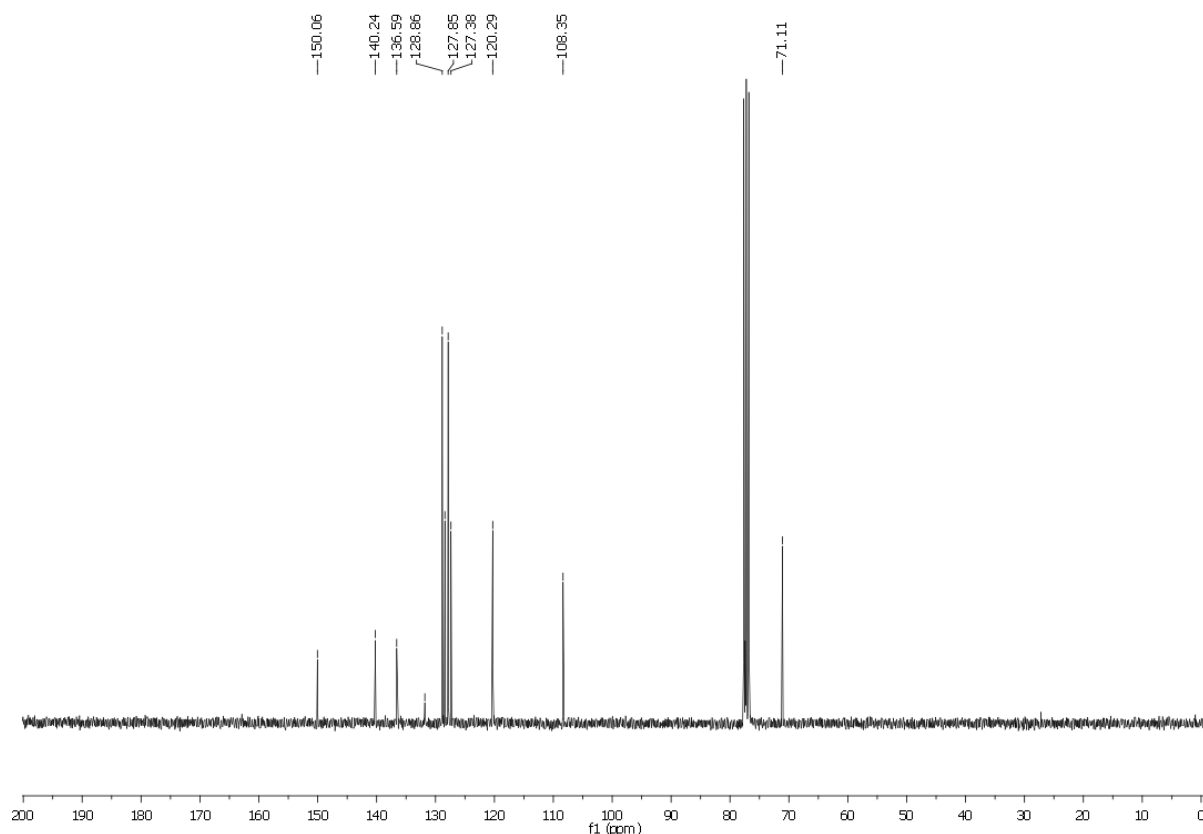
**Two-step procedure for the synthesis of 3e: 4-Benzyloxy-2-nitroaniline (4e).** A suspension of **2e** (10.5 mmol, 3.00 g) in hydrochloric acid (4 N, 9 mL) and ethanol (18 mL) was heated to reflux for six hours. The solution was cooled to ambient temperature, and an aqueous solution of concentrated ammonia (7.2 mL) was added. The solid was filtered off, washed with cold water and dried under vacuum to give 4-benzyloxy-2-nitroaniline (**4e**) as a red solid in 86 % (9.0 mmol, 2.2 g) yield, mp 142°C (reported in the literature:<sup>13</sup> 143°C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.63 (d, *J* = 2.9, 1H), 7.48 – 7.26 (5H), 7.11 (dd, *J* = 2.9, 9.1, 1H), 6.74 (d, *J* = 9.1, 1H), 5.87 (s(br.), 2H), 5.01 (s, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 150.1, 140.2, 136.6, 131.8, 128.9, 128.4, 127.9, 127.4, 120.3, 108.4, 71.1; IR (KBr-disc) ν 3477 (s), 3354 (s), 1570 (s), 1414 (s), 1217 (s); MS (ESI) *m/z* 145 (64 %), 155 (51 %), 245 (100 %); HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 245.0926, found 245.0941; Anal. calcd for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>: C, 63.9 %; H, 5.0 %; N, 11.5 %; found C, 63.8 %; H, 4.9 %; N, 11.7 %.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of **4e**



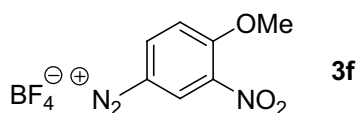
<sup>13</sup> Wiegrebbe, W.; Faber, L.; Budzikiewicz, H. *Liebigs Ann. Chem.* **1970**, 733, 125-140.

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) of **4e**



**Synthesis of 4-Benzyloxy-2-nitrobenzenediazonium tetrafluoroborate (3e) from 4e:** A solution of **2e** (1.6 mmol, 400 mg) in diethylether/ acetonitrile (2:1, 10 mL) was cooled to  $-15^{\circ}\text{C}$ .  $\text{BF}_3\cdot\text{OEt}_2$  (2.5 mmol, 0.31 mL) was added, and the solution was stirred at this temperature for 15 minutes. A solution of *tert*-butyl nitrite (2.0 mmol, 0.24 mL) in diethylether (5 mL) was added to the reaction mixture over a period of 10 minutes. Stirring at  $-15^{\circ}\text{C}$  was continued for one hour. The suspension was filtered, and the precipitate was washed with cold ethanol and cold MTBE to give 4-benzyloxy-2-nitrobenzenediazonium tetrafluoroborate (**3e**) as a pale solid in 90 % (1.5 mmol, 506 mg) yield. All analytical data are identical to those reported above for compound **3e** obtained via Procedure C2.

C8 4-Methoxy-3-nitrobenzenediazonium tetrafluoroborate (**3f**)

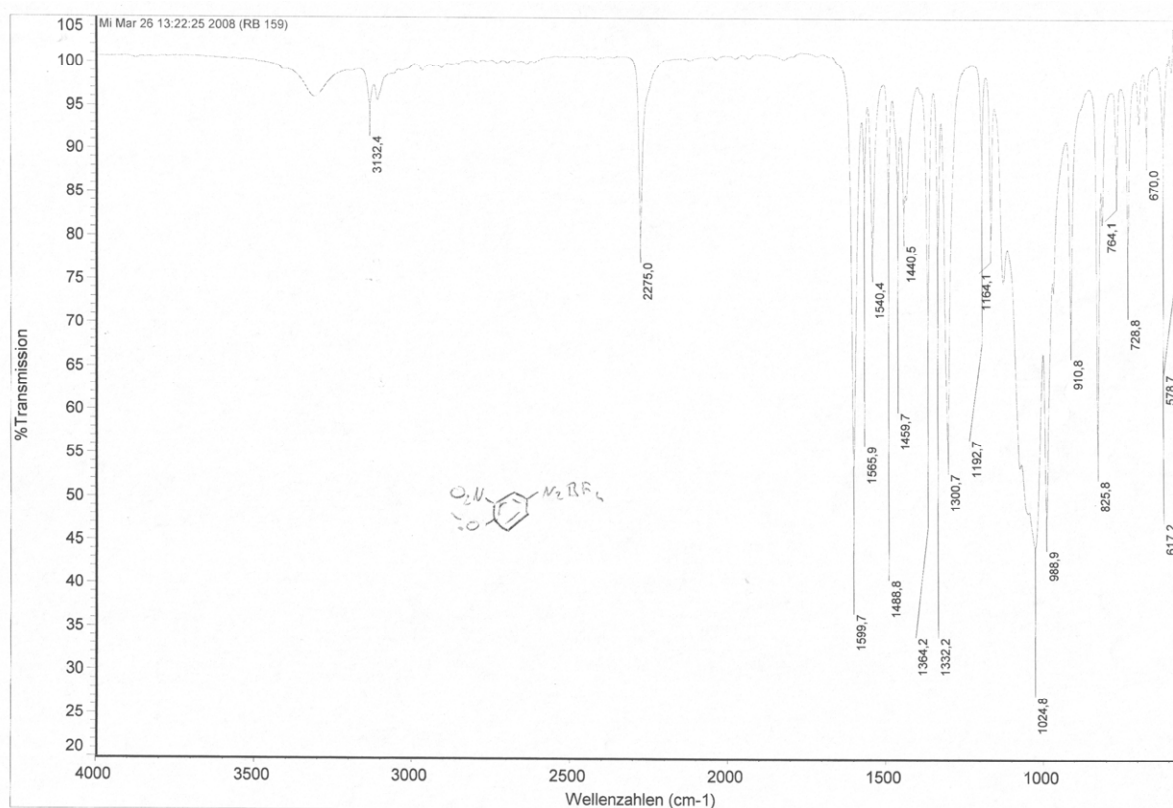


**Procedure C1:** Obtained from **2f** (1.00 g, 4.8 mmol). Yield: 32% (0.40 g, 1.5 mmol).

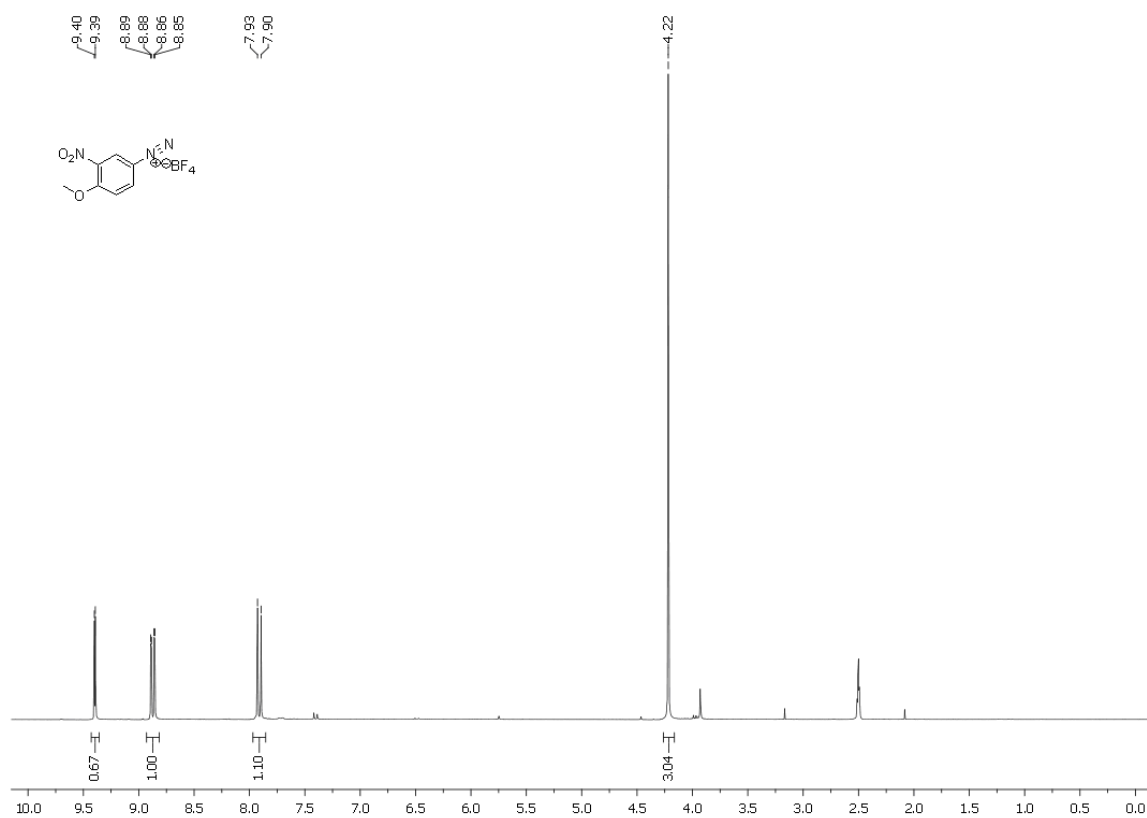
**Procedure C2:** Obtained from **2f** (637 mg, 3.0 mmol). Yield: 72% (590 mg, 2.2 mmol).

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  9.40 (d,  $J = 2.6$ , 1H), 8.87 (dd,  $J = 2.6, 9.6$ , 1H), 7.91 (d,  $J = 9.6$ , 1H), 4.22 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  161.3, 139.0, 138.3, 131.6, 117.8, 104.8, 59.3; IR (KBr disc)  $\nu$  3132 (m), 2275 (s,  $\text{N}_2$ ), 1599 (s), 1540 (s), 1300 (s); MS (ESI)  $m/z$  180 (100 %), 152 (12 %); HRMS (ESI)  $m/z$  calcd for  $\text{C}_7\text{H}_6\text{N}_3\text{O}_3^+ [\text{M}]^+$ : 180.0409, found 180.0416.

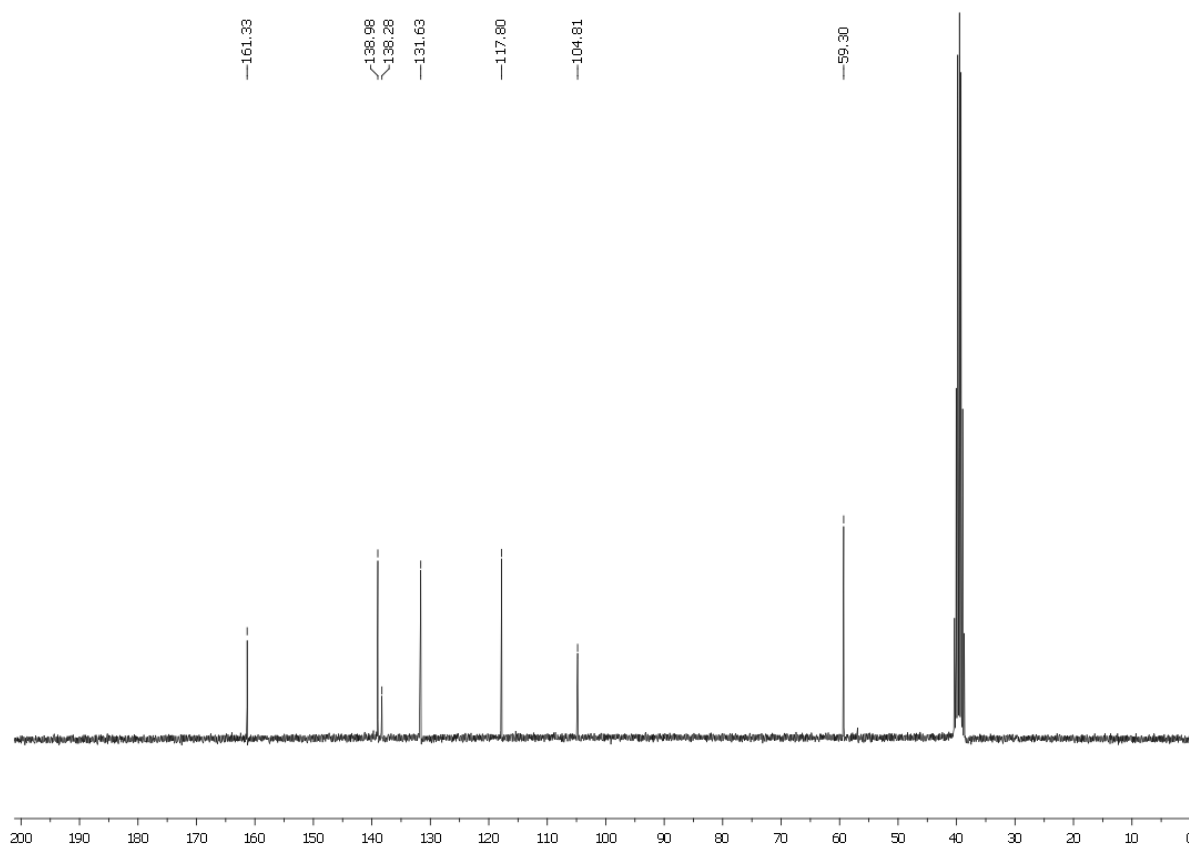
IR (KBr-disc)



$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )

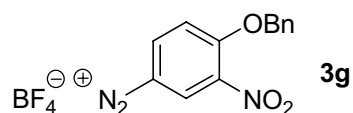


$^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )





C9 4-Benzyloxy-3-nitrobenzenediazonium tetrafluoroborate (**3g**)

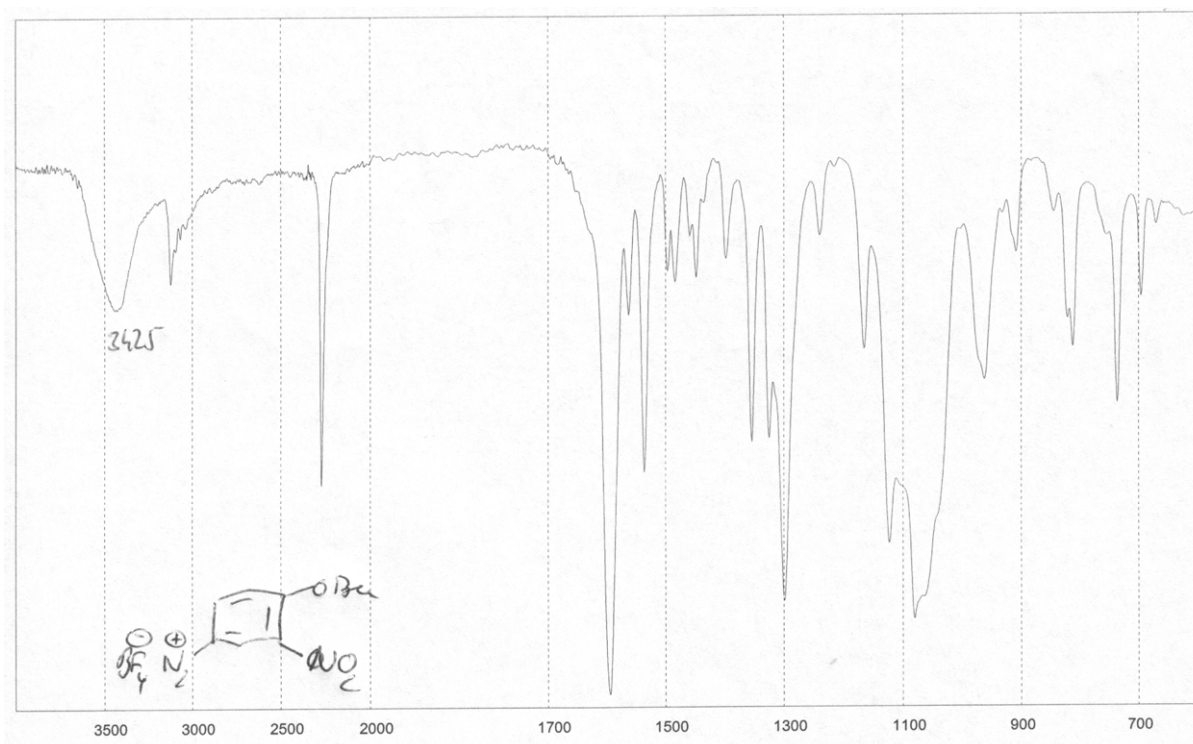


**Procedure C1:** Obtained from **2g** (0.30 g, 1.1 mmol). Yield: 58% (0.21 g, 0.6 mmol).

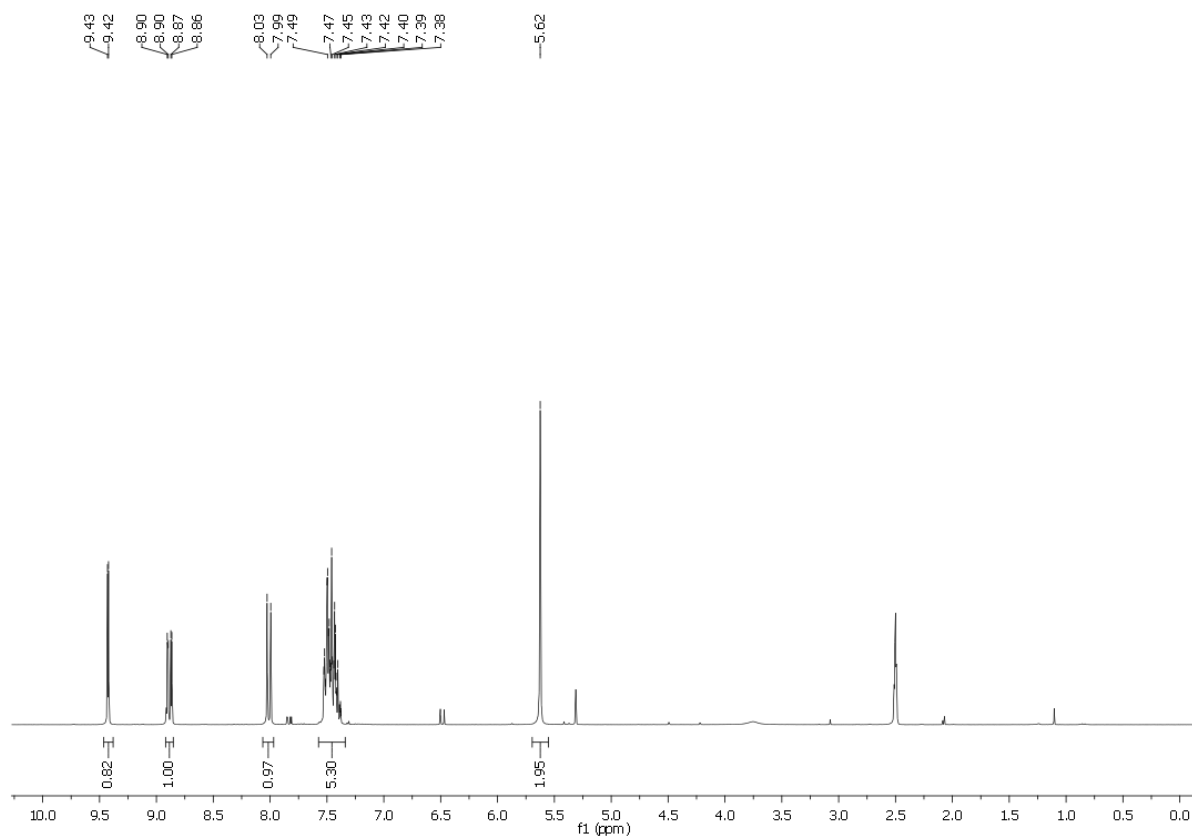
**Procedure C2:** Obtained from **2g** (867 mg, 3.0 mmol). Yield: 83% (862 mg, 2.5 mmol).

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  9.43 (d,  $J = 2.5$ , 1H), 8.89 (dd,  $J = 2.5$ , 9.5, 1H), 8.01 (d,  $J = 9.5$ , 1H), 7.55 – 7.29 (m, 5H), 5.62 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  160.2, 138.9, 138.5, 134.1, 131.7, 128.8, 128.7, 127.9, 118.5, 105.1, 73.1; IR (KBr-disc)  $\nu$  3425 (m), 2271 (s,  $\text{N}_2$ ), 1594 (s), 1563 (s), 1299 (s); MS (ESI)  $m/z$  256 (100 %), 239 (11 %), 182 (16 %), 91 (71 %); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{10}\text{N}_3\text{O}_3^+ [\text{M}]^+$ : 256.0722, found 256.0742.

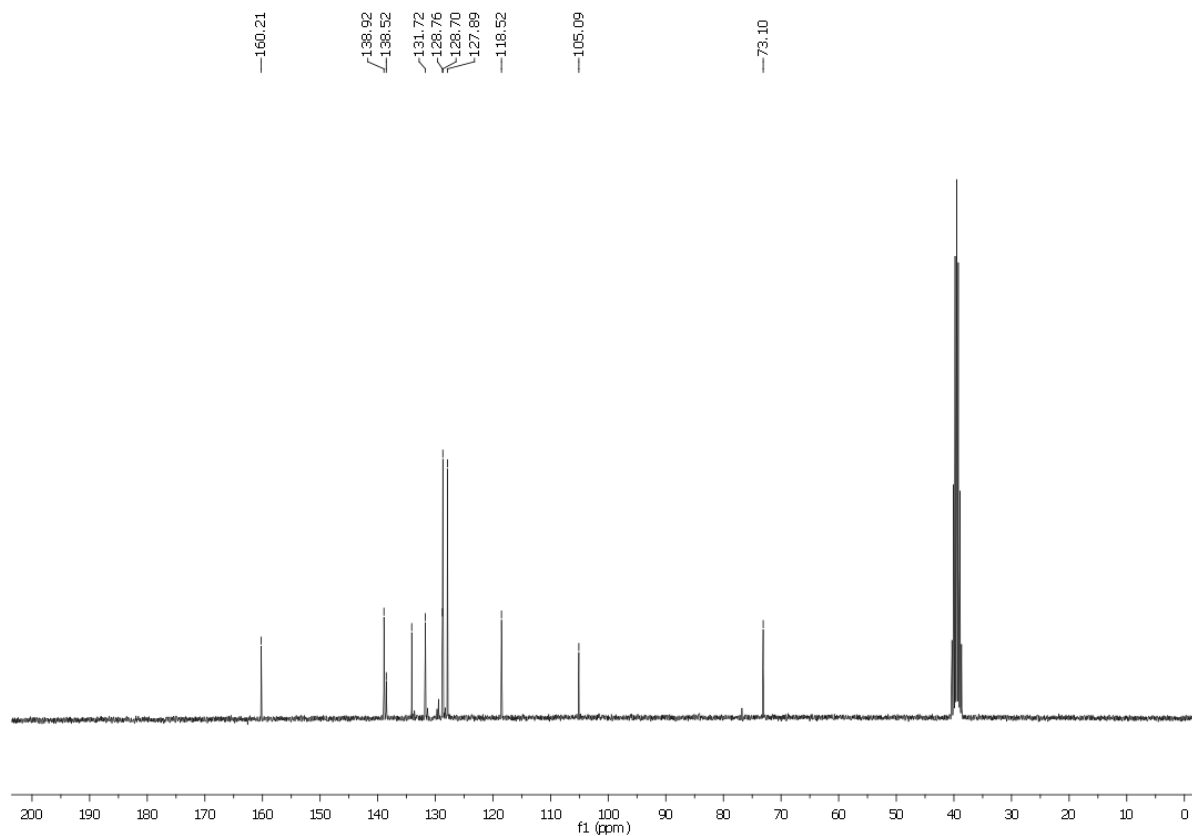
IR (KBr-disc)



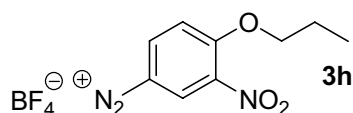
$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )



$^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )



C10 3-Nitro-4-propoxybenzenediazonium tetrafluoroborate (**3h**)

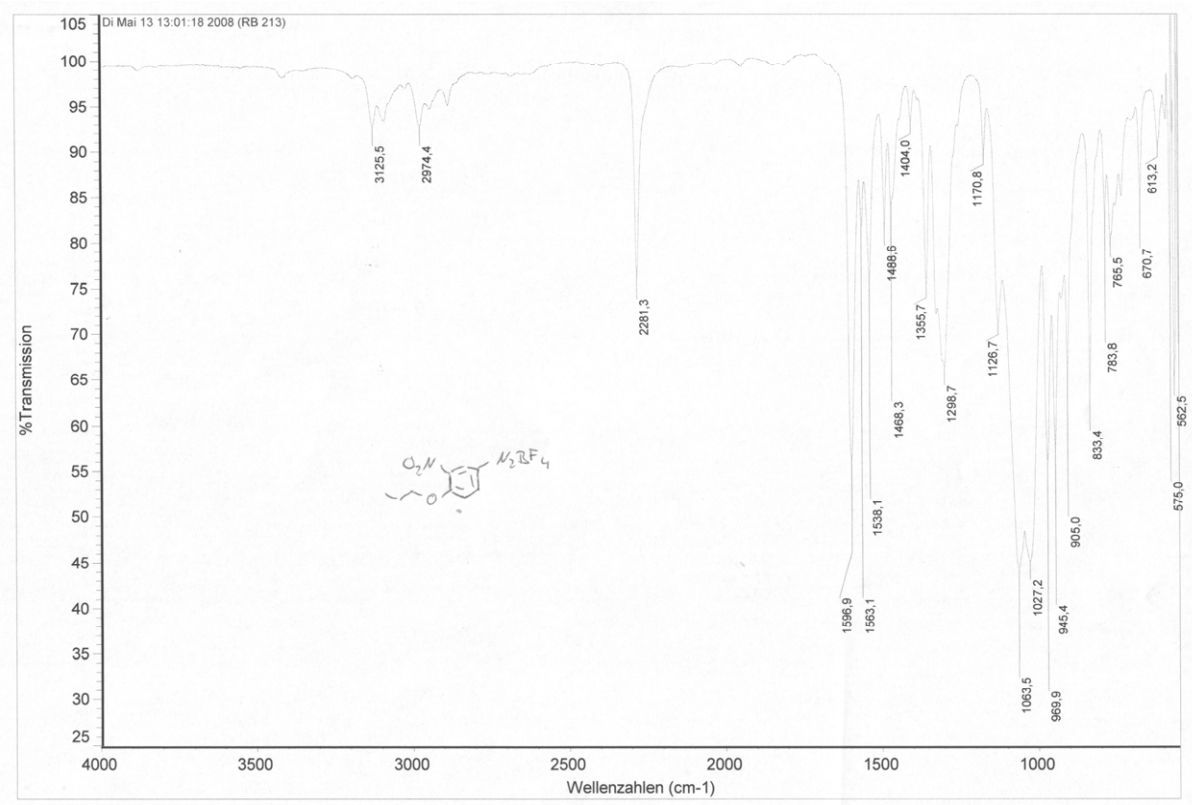


**Procedure C1:** Obtained from **2h** (0.50 g, 2.1 mmol). Yield: 68% (0.42 g, 1.8 mmol).

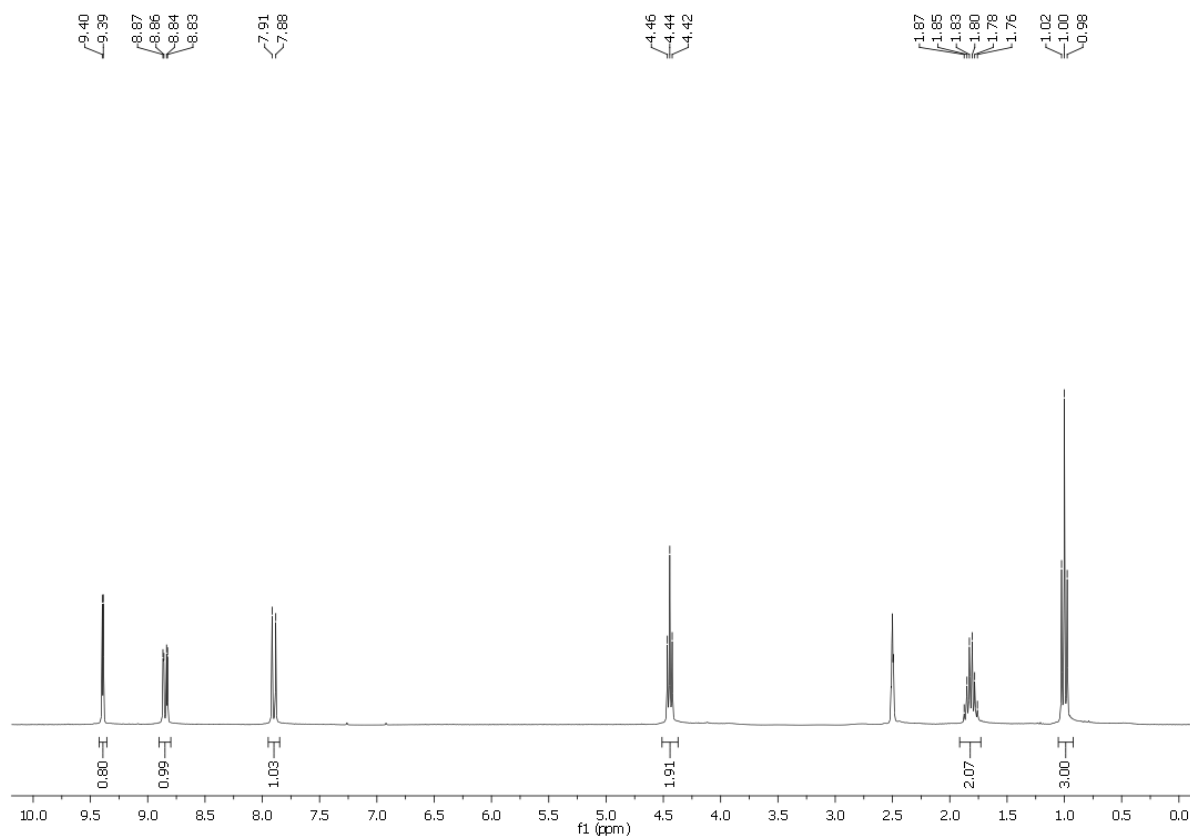
**Procedure C2:** Obtained from **2h** (722 mg, 3.0 mmol). Yield: 66% (590 mg, 2.0 mmol).

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  9.39 (d,  $J = 2.6$ , 1H), 8.85 (dd,  $J = 2.6$ , 9.5, 1H), 7.90 (d,  $J = 9.6$ , 1H), 4.44 (t,  $J = 6.3$ , 2H), 1.82 (tq,  $J = 6.3$ , 7.4, 2H), 1.00 (t,  $J = 7.4$ , 3H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  160.7, 139.0, 138.4, 131.7, 118.2, 104.5, 73.6, 21.4, 10.0; IR (KBr-disc)  $\nu$  3125 (m), 2974 (m), 2281 (s,  $\text{N}_2$ ), 1596 (s), 1355 (s); MS (ESI)  $m/z$  208 (100 %), 180 (28 %), 138 (51 %), 91 (16 %); HRMS (ESI)  $m/z$  calcd for  $\text{C}_9\text{H}_{10}\text{N}_3\text{O}_3^+$   $[\text{M}]^+$ : 208.0722, found 208.0718.

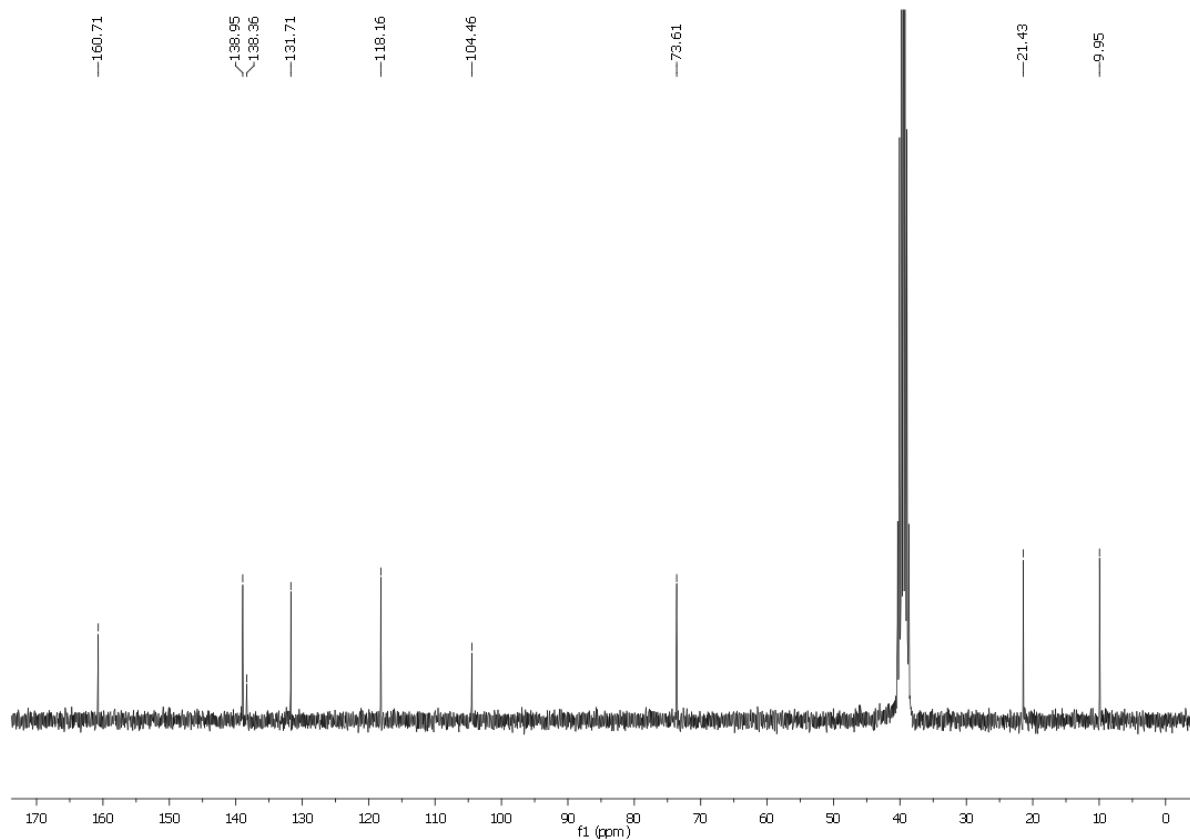
IR (KBr-disc)



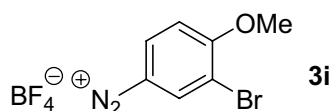
$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )



$^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )



C11 3-Bromo-4-methoxybenzenediazonium tetrafluoroborate (**3i**)

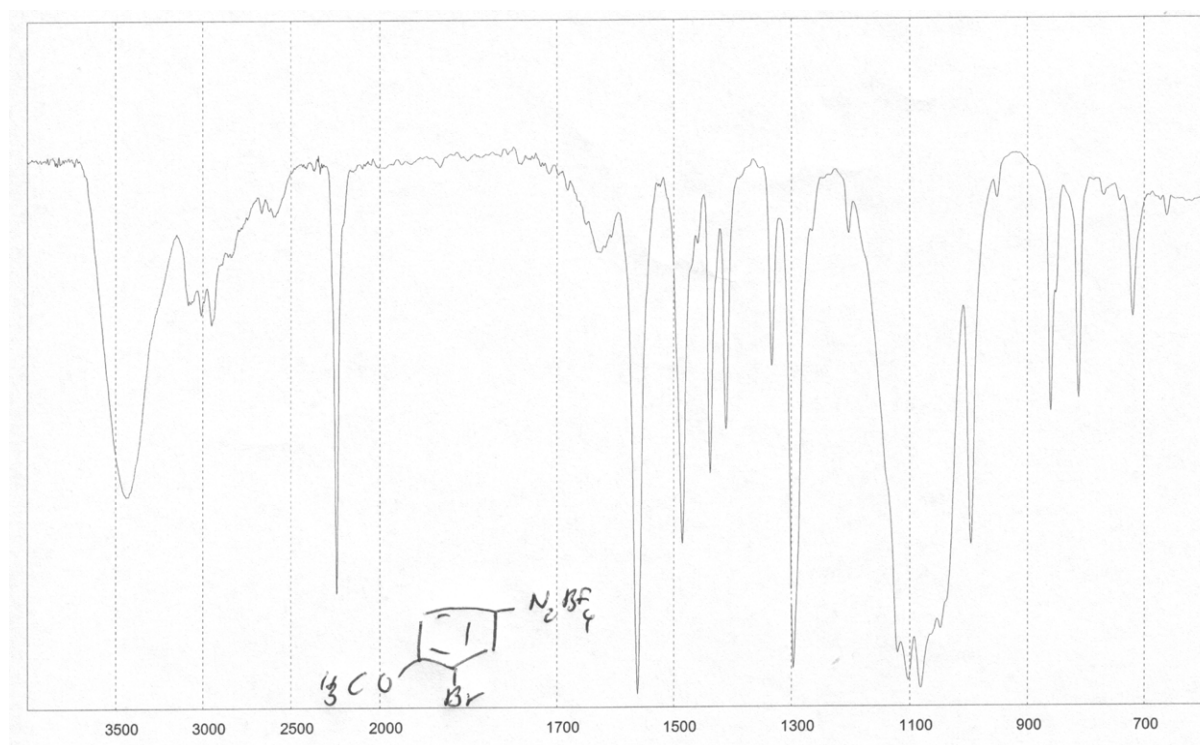


**Procedure C1:** Obtained from **2i** (0.50 g, 2.1 mmol). Yield: 25% (0.15 g, 0.5 mmol).

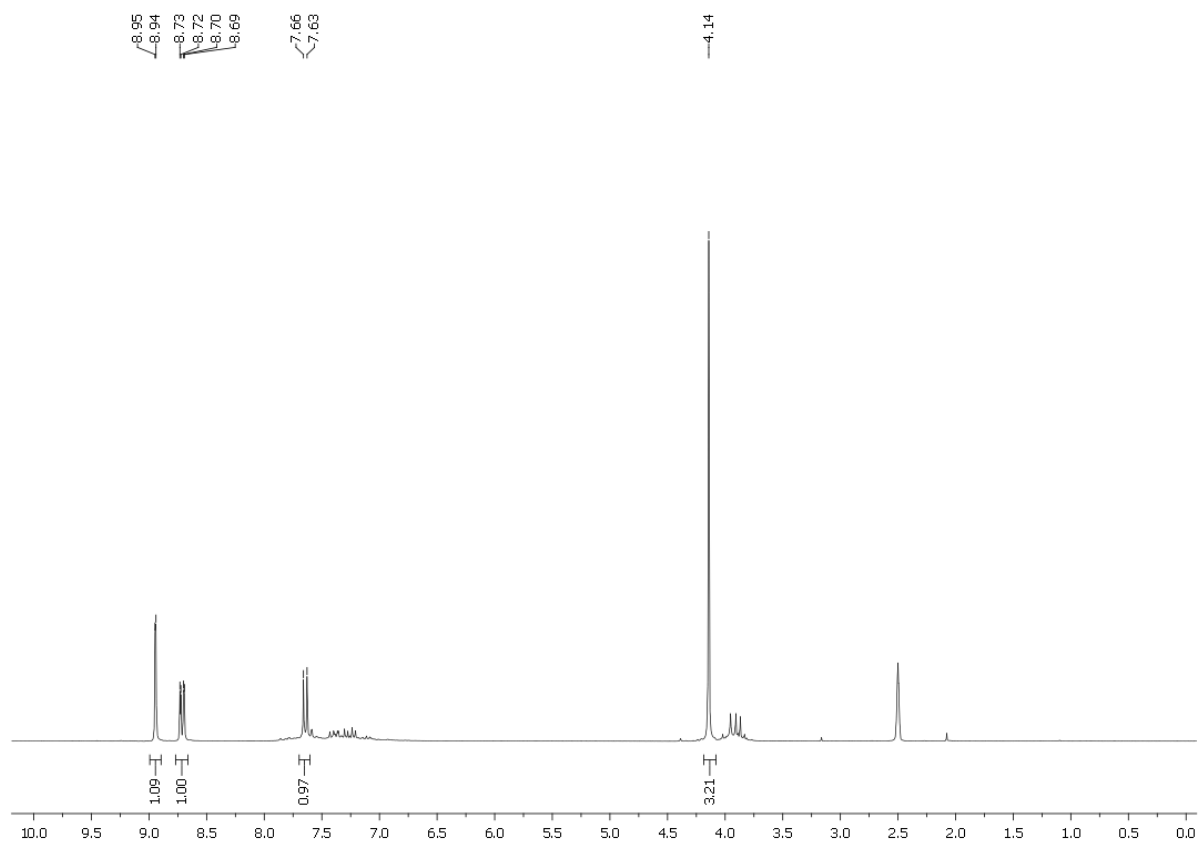
**Procedure C2:** Obtained from **2i** (739 mg, 3.0 mmol). Yield: 39% (590 mg, 1.2 mmol).

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.96 (d,  $J = 2.5$ , 1H), 8.72 (dd,  $J = 2.5, 9.3$ , 1H), 7.65 (d,  $J = 9.3$ , 1H), 4.15 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  165.3, 136.6, 136.1, 114.7, 111.7, 104.8, 58.7; IR (KBr-disc)  $\nu$  3439 (m), 2241 (s,  $\text{N}_2$ ), 1562 (s), 1485 (s), 1297 (s); MS (ESI)  $m/z$  185 (100%), 170 (6%), 155 (17%), 91 (2%); HRMS (ESI)  $m/z$  calcd for  $\text{C}_7\text{H}_6\text{BrN}_2\text{O}^+$   $[\text{M}]^+$ : 212.9663, found: 212.9678.

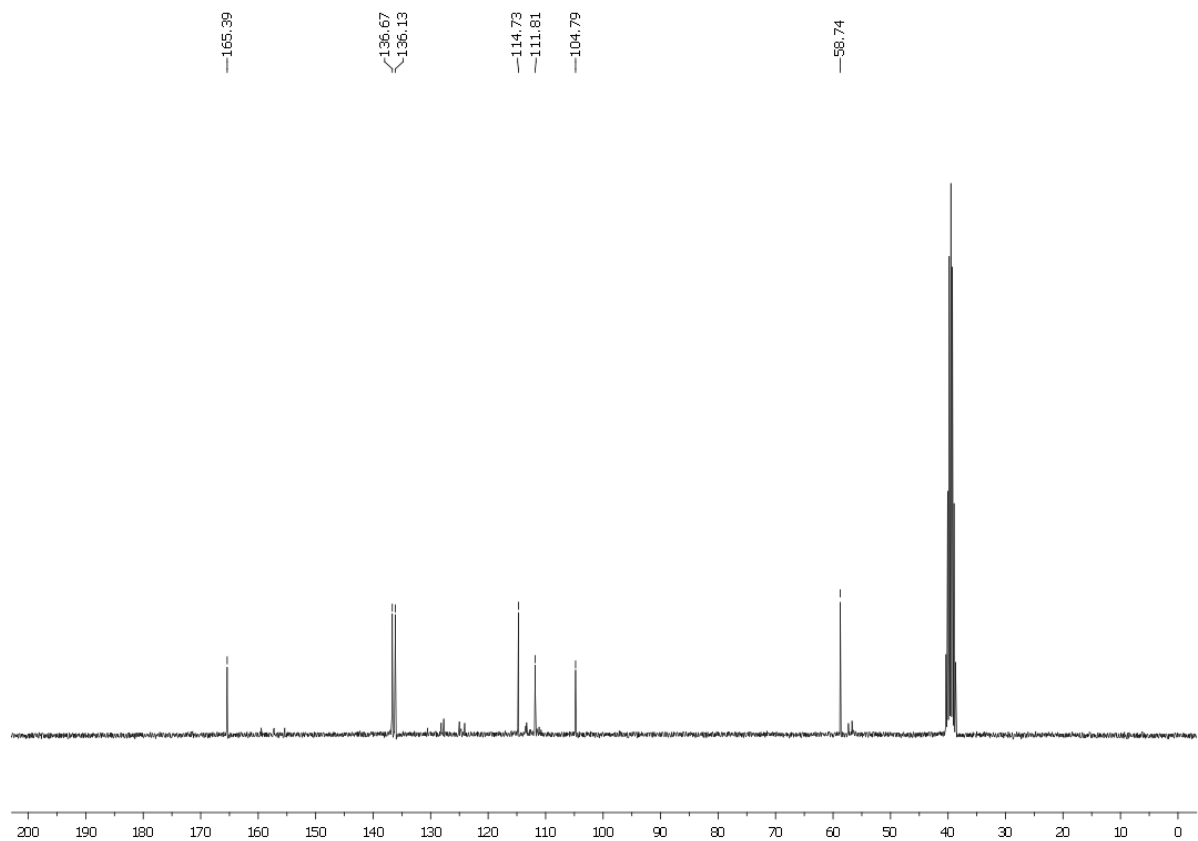
IR (KBr-disc)



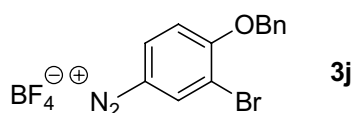
$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )



$^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )



C12 4-Benzyloxy-3-bromobenzenediazonium tetrafluoroborat (**3j**)

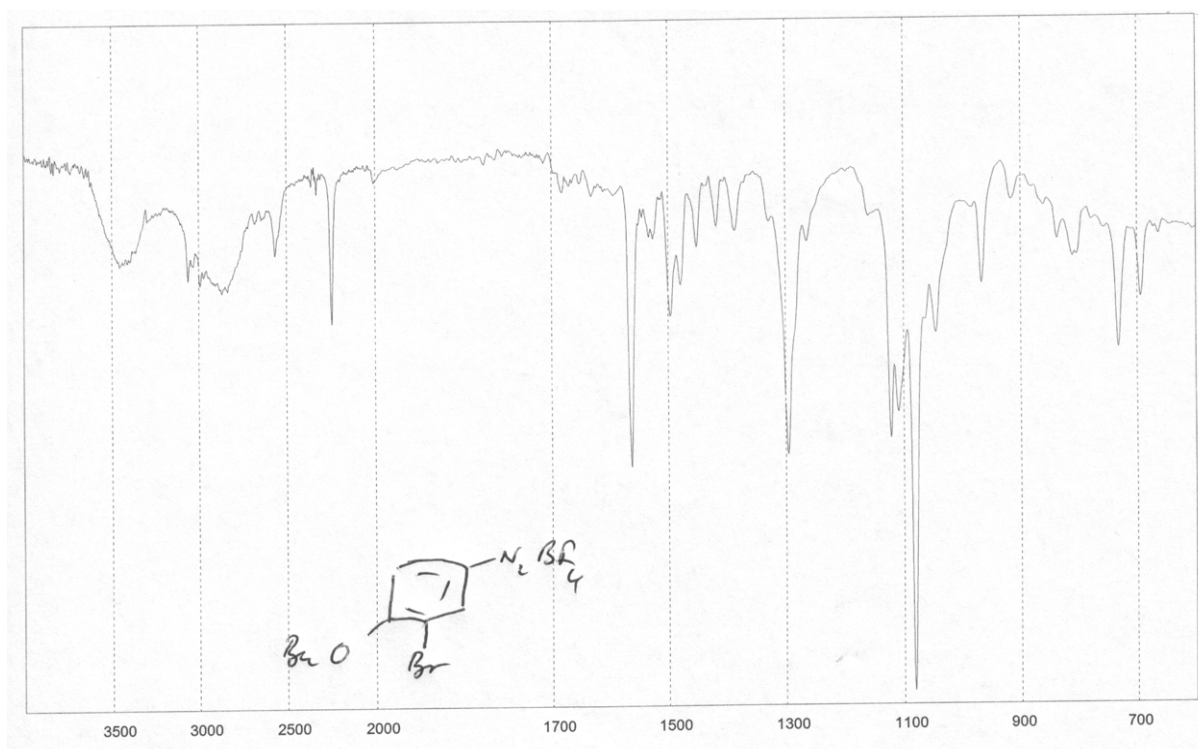


**Procedure C1:** Obtained from **2j** (0.40 g, 1.3 mmol). Yield: 52% (0.25 g, 0.7 mmol).

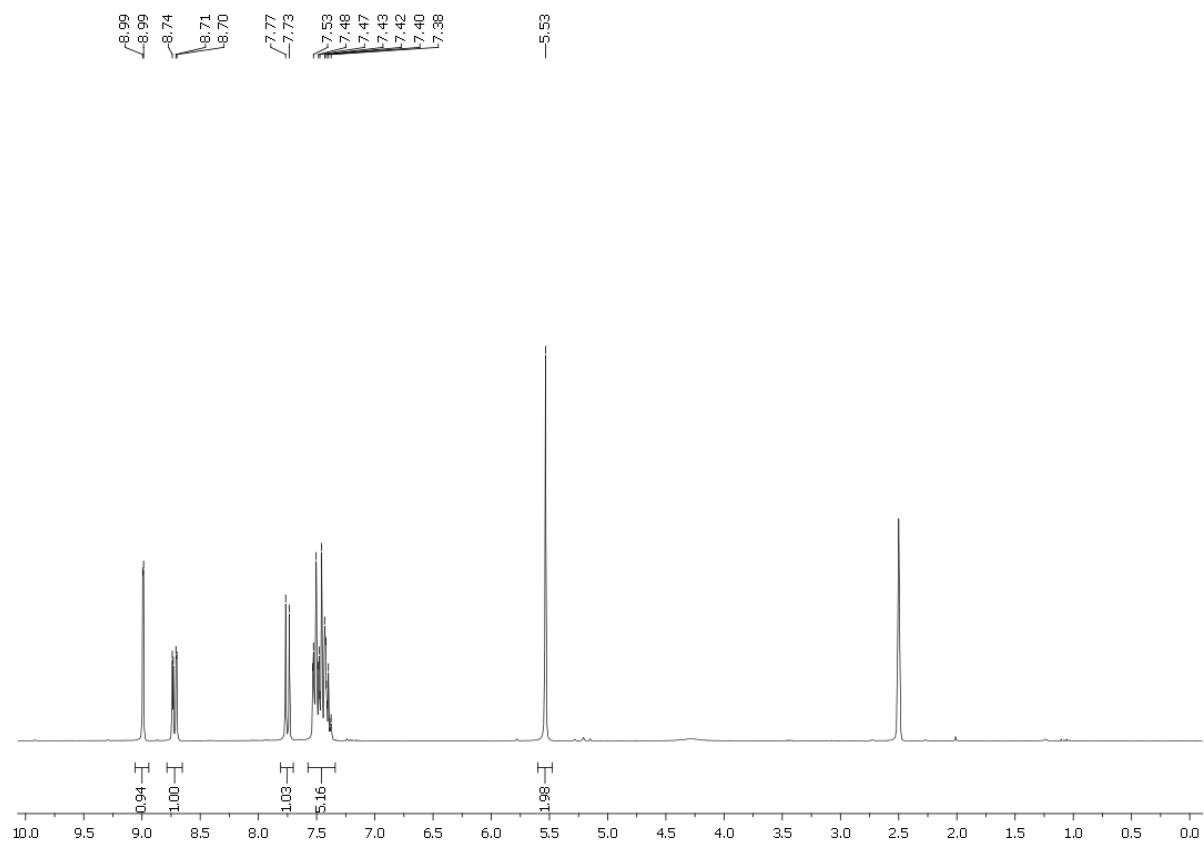
**Procedure C2:** Obtained from **2j** (969 mg, 3.0 mmol). Yield: 66% (750 mg, 2.0 mmol).

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.99 (d,  $J = 2.5$ , 1H), 8.72 (dd,  $J = 2.5, 9.4$ , 1H), 7.75 (d,  $J = 9.4$ , 1H), 7.57 – 7.34 (5H), 5.53 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  164.3, 136.79, 135.9, 134.6, 128.7, 128.7, 127.9, 115.58, 112.2, 105.1, 72.4; IR (KBr-disc)  $\nu$  3454 (m), 2972 (m), 2243 (s,  $\text{N}_2$ ), 1563 (s), 1296 (s); MS (ESI)  $m/z$  289 (19 %), 261 (24 %), 185 (6 %), 91 (100 %); HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{10}\text{BrN}_2\text{O}^+ [\text{M}]^+$ : 288.9976, found 288.9991.

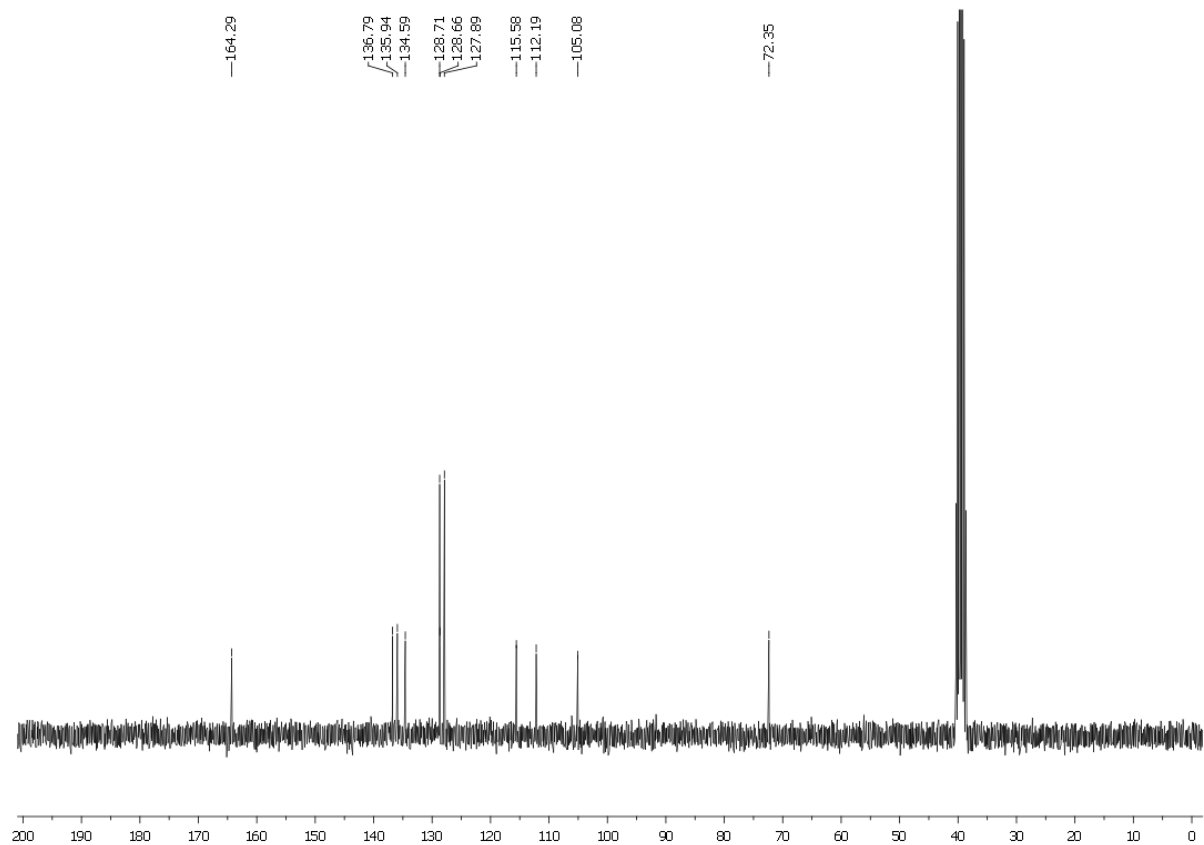
IR (KBr-disc)



$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )



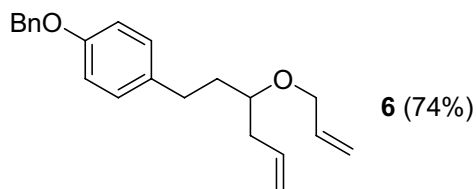
$^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )





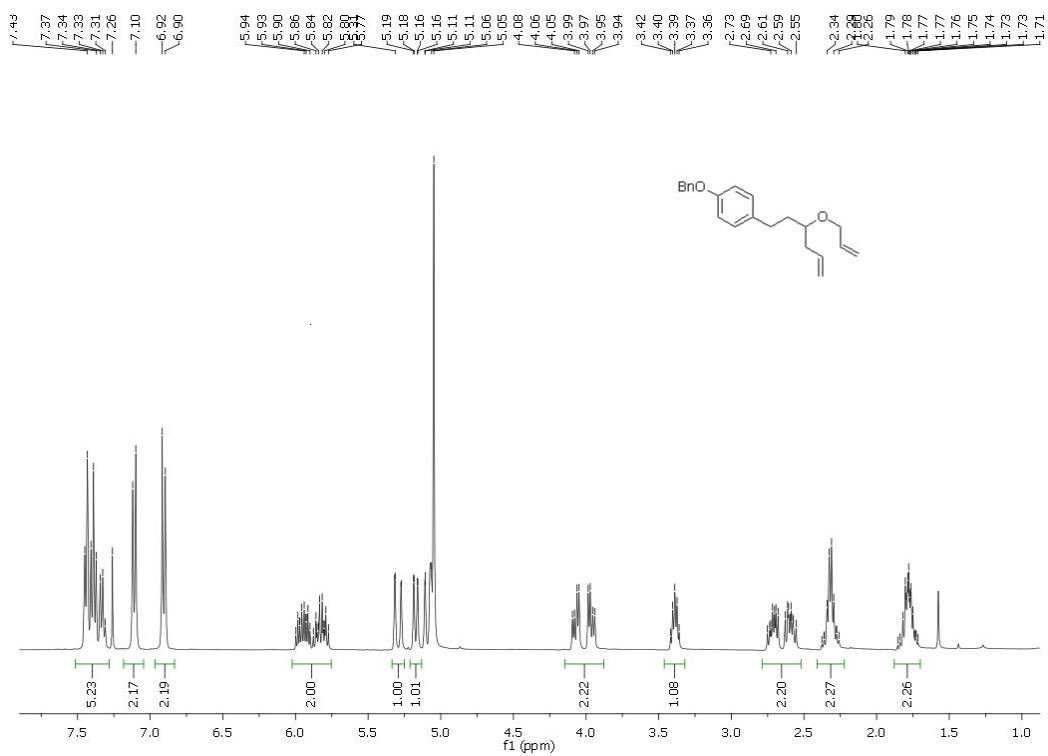
## D Experimental procedures, analytical data and copies of spectra for the synthesis of de-O-methyl centrolobine and all intermediates

### D1 1-(3-(Allyloxy)hex-5-enyl)-4-(benzyloxy)benzene (**6**)

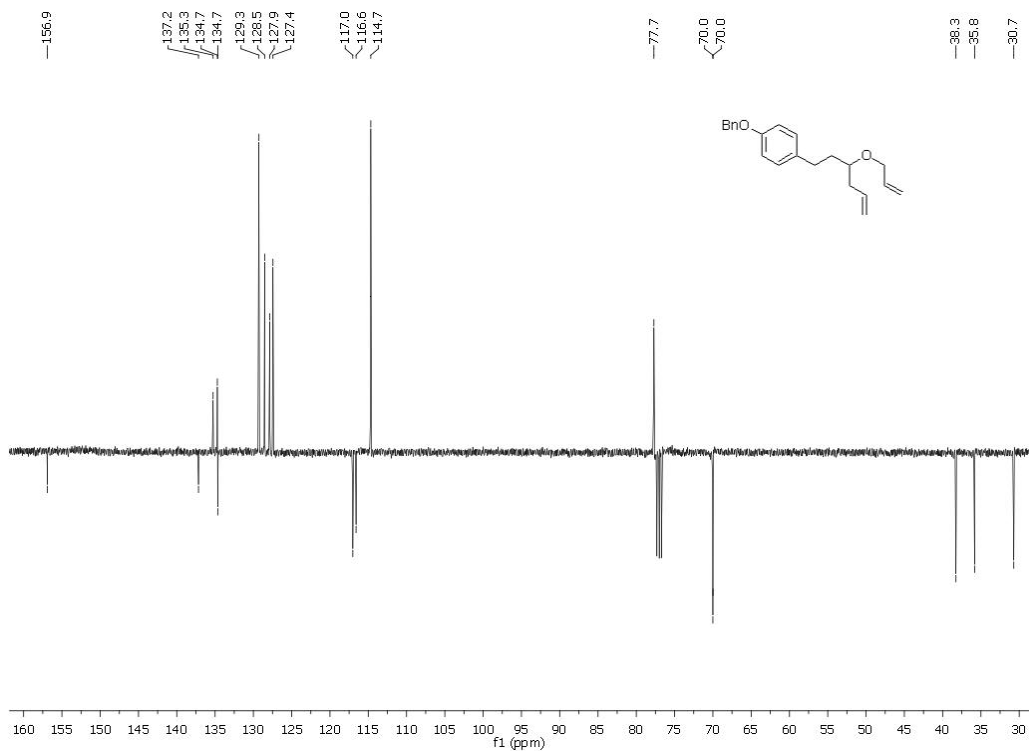


To a solution of homoallylic alcohol **5** (1.91 g, 6.8 mmol) in dry and degassed THF (30 mL) was added NaH (60% dispersion in mineral oil, 300 mg, 7.5 mmol). The mixture was heated to reflux for 30 min., cooled to ambient temperature, and allyl bromide (0.71 mL, 8.2 mmol) was added dropwise. The mixture was again heated to reflux for one hour, then cooled to ambient temperature and quenched by addition of water (25 mL). It was extracted with diethyl ether (100 mL), and the organic layer was separated, dried with MgSO<sub>4</sub>, filtered and evaporated. The residue was purified by flash chromatography on silica to give the title compound **6** as a colourless liquid in 74% (1.63 g, 5.0 mmol) yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.31 (5H), 7.11 (d, *J* = 8.5, 2H), 6.91 (d, *J* = 8.6, 2H), 5.95 (dddd, *J* = 5.6, 5.6, 10.4, 17.2 1H), 5.82 (dddd, *J* = 7.1, 7.2, 10.2, 17.2 1H), 5.29 (ddm, *J* = 1.6, 17.2, 1H), 5.17 (ddm, *J* = 1.3, 10.3, 1H), 5.11 – 5.06 (2H), 5.05 (s, 2H), 4.07 (dd, *J* = 5.6, 12.6, 1H), 3.96 (dd, *J* = 5.6, 12.6, 1H), 3.39 (m, 1H), 2.66 (ddd, *J* = 5.9, 9.3, 13.6, 1H), 2.59 (ddd, *J* = 5.9, 9.3, 13.6, 1H), 2.40-2.27 (2H), 1.86-1.73 (2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, APT) δ 156.9, 136.9, 134.9, 134.4, 134.3, 129.0, 128.2, 127.5, 127.1, 116.7, 116.3, 114.4, 77.4, 69.7, 69.7, 38.0, 35.5, 30.4; IR (NaCl-film): ν 2930 (w), 2860 (w), 1610 (w), 1510 (s), 1454 (w), 1240 (s), 1078 (m); LRMS (FAB) *m/z* 322 (13 %) [M + H]<sup>+</sup>, 257 (16 %); HRMS (FAB) *m/z* calcd. for C<sub>22</sub>H<sub>26</sub>O<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup>: 322.1933, found 322.1964; Anal. calcd. for C<sub>22</sub>H<sub>26</sub>O<sub>2</sub>: C, 81.9 %; H, 8.1 %; found C, 81.4 %; H, 9.0 %.

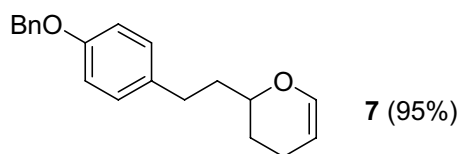
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , APT)

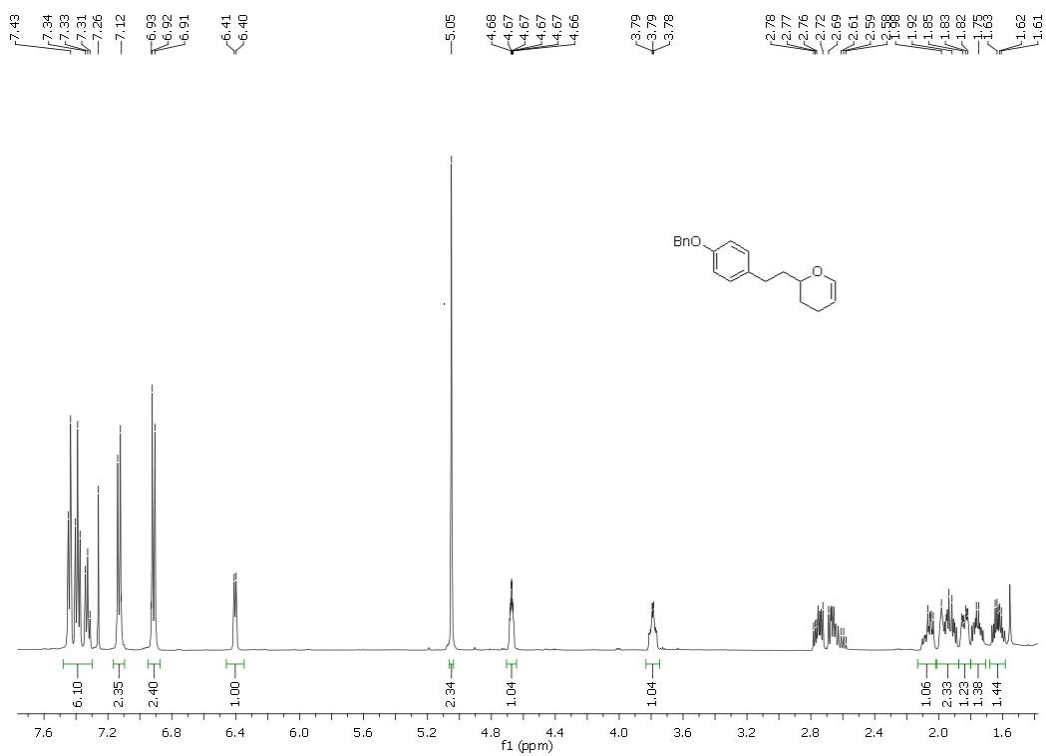


D2 2-(4-(Benzyloxy)phenethyl)-3,4-dihydro-2H-pyran (7)

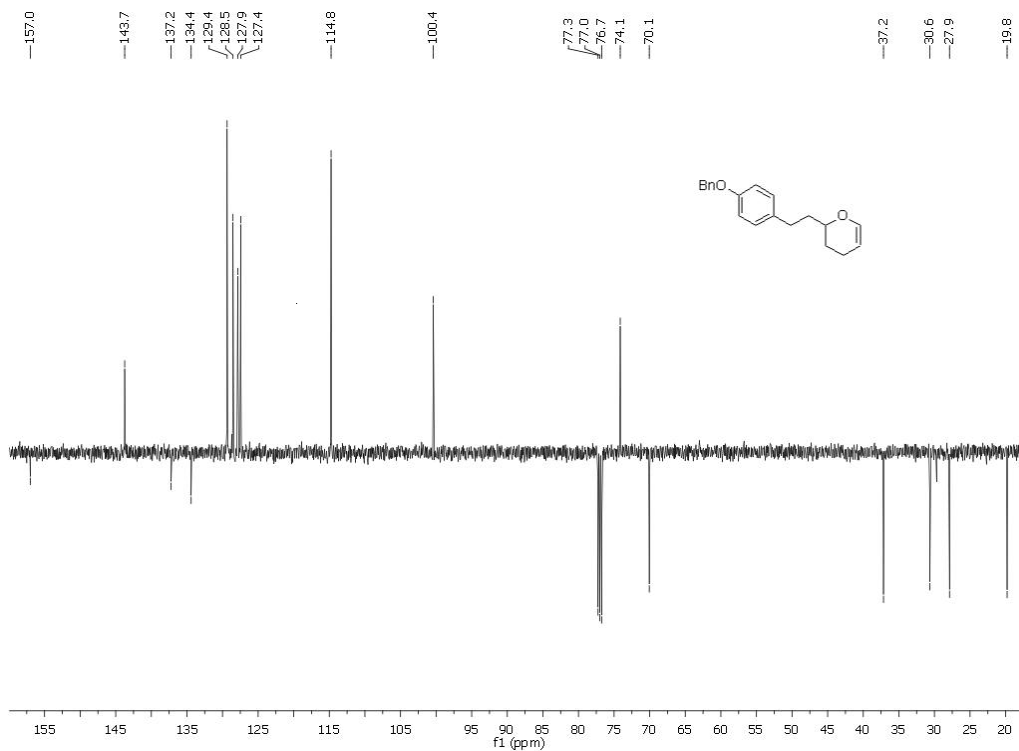


To a solution of **6** (0.99 g, 3.1 mmol) in dry and degassed toluene (25 mL) was added  $[\text{Cl}_2(\text{PCy}_3)_2\text{RuCHPh}]$  (125 mg, 5 mol %) under an atmosphere of dry argon. The solution is heated to 90°C for two hours, resulting in complete conversion of the starting material. 2-Propanol (3 mL) and solid NaOH (32 mg, 0.8 mmol) were added, and heating to reflux was continued for two hours. TLC revealed complete consumption of the intermediate metathesis product and formation of the cyclic enol ether. All volatiles were evaporated, and the residue was purified by flash chromatography on silica (eluent cyclohexane/MTBE 10 : 1) to give the title compound **7** in 95 % (0.87 g, 2.9 mmol) yield. This material is sufficiently pure for further transformations. If required, further purification is possible by recrystallization from cyclohexane, mp 38°C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 – 7.37 (5H), 7.13 (d,  $J = 8.6$ , 2H), 6.91 (d,  $J = 8.6$ , 2H), 6.40 (d,  $J = 6.1$ , 1H), 5.05 (s, 2H), 4.67 (ddd,  $J = 2.4, 4.8, 6.1$ , 1H), 3.79 (m, 1H), 2.75 (dddd,  $J = 5.5, 5.5, 9.8, 9.8$ , 1H), 2.66 (dddd,  $J = 6.9, 9.5, 10.4, 13.9$  1H), 2.06 (m, 1H), 1.99 – 1.89 (2H), 1.85 (m, 1H), 1.76 (m, 1H), 1.63 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.0, 143.7, 137.2, 134.4, 129.4, 128.5, 127.9, 127.4, 114.7, 100.4, 74.1, 70.1, 37.2, 30.6, 27.9, 19.8; IR (KBr-disc)  $\nu$  3052 (m), 3029 (m), 2928 (m), 2847 (w), 1649 (s), 1610 (m), 1581 (w), 1512 (s), 1453(s), 1383 (m), 1297 (w), 1176 (w), 1053 (m), 1023 (m); LRMS (FAB)  $m/z$  294 ( $[\text{M}]^+$ , 14 %), 197 (12 %), 91 (100 %); HRMS (FAB)  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{22}\text{O}_2$   $[\text{M}]^+$  294.1620, found 294.1631; Anal. calcd. for  $\text{C}_{20}\text{H}_{22}\text{O}_2$ : C, 81.6 %; H, 7.5 %; found C, 81.0 %; H, 7.7 %.

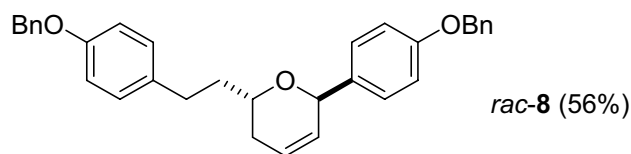
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )

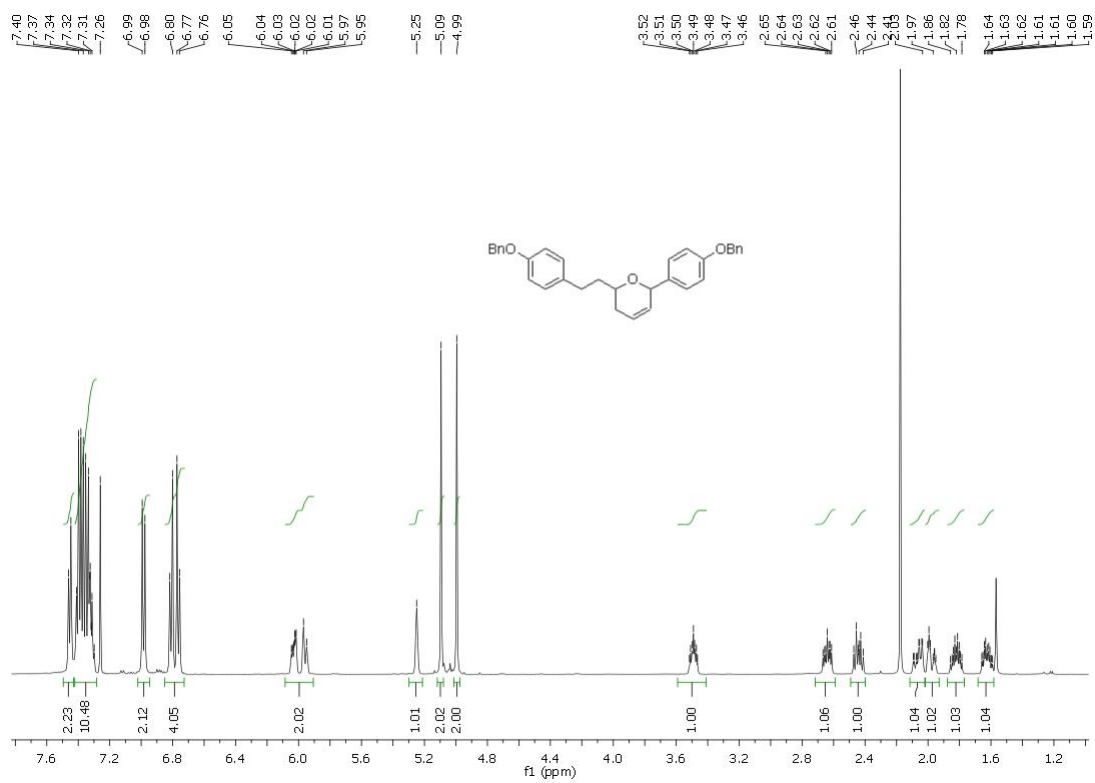


D3 (2*SR*,6*RS*)-2-(4-(Benzyloxy)phenethyl)-6-(4-(benzyloxy)phenyl)-3,6-dihydro-  
2*H*-pyran (*rac*-**8**)

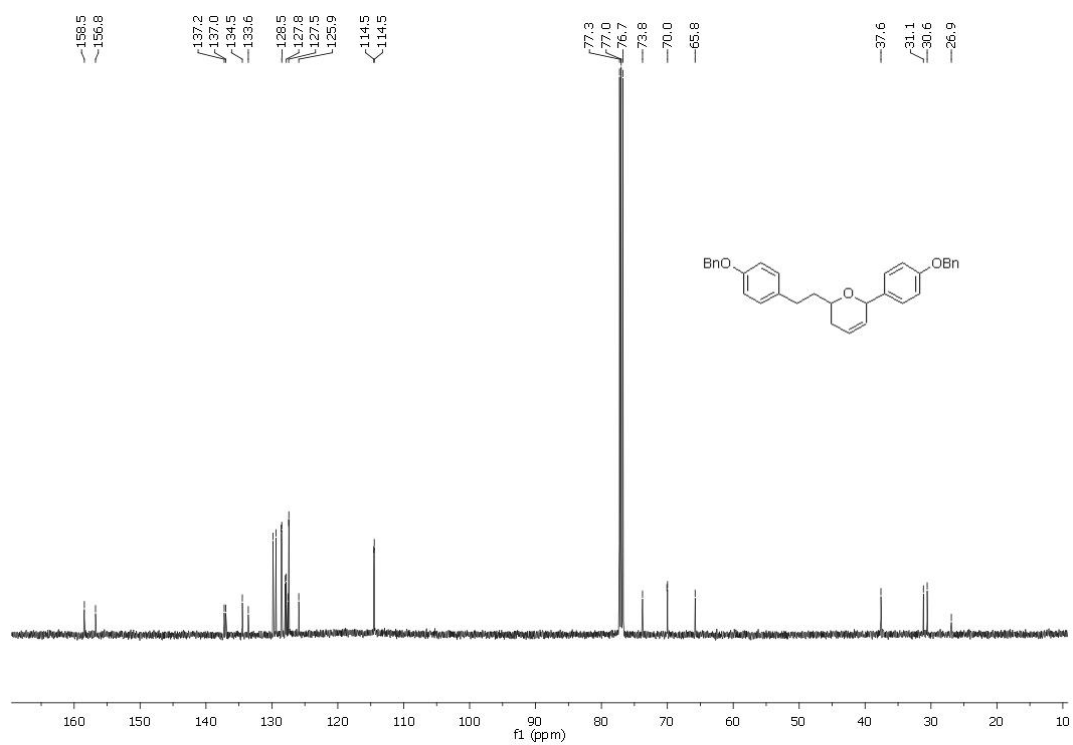


To a solution of enol ether **7** (422 mg, 1.4 mmol) and diazonium salt **3b** (512 mg, 1.7 mmol) in acetonitrile (10 mL) was added NaOAc (469 mg, 5.7 mmol), followed by Pd<sub>2</sub>(dba)<sub>3</sub>•CHCl<sub>3</sub> (30 mg, 2 mol%). Immediately after the Pd-catalyst was added, an evolution of gas was observed, which ceased after approximately 3 hours. The mixture was concentrated, and all inorganics were removed by filtration of the mixture over a short pad of silica. The silica pad was thoroughly washed with MTBE, and all volatiles were removed in vacuo. The residue was purified by recrystallization from cyclohexane-diethyl ether, to give the title compound *rac*-**8** in 56% (0.37 g, 0.8 mmol) yield as colourless crystals, mp 99°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.45 (d, *J* = 7.3, 2H), 7.41 – 7.30 (10H), 6.98 (d, *J* = 8.6, 2H), 6.81 (d, *J* = 8.6, 1H), 6.76 (d, *J* = 8.6, 1H), 6.03 (ddm, *J* = 5.0, 10.2, 1H), 5.96 (dm, *J* = 10.2, 1H), 5.25 (s(br), 1H), 5.09 (s, 2H), 4.99 (s, 2H), 3.49 (m, 1H), 2.64 (ddd, *J* = 4.7, 8.6, 13.7, 1H), 2.44 (ddd, *J* = 8.2, 8.2, 13.8, 1H), 2.07 (ddm, *J* = 9.6, 17.5, 1H), 1.97 (ddd, *J* = 4.0, 4.0, 17.6, 1H), 1.82 (dddd, *J* = 5.0, 8.7, 8.7, 13.8, 1H), 1.62 (dddd, *J* = 3.6, 8.7, 8.7, 13.3, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 158.5, 156.8, 137.2, 137.0, 134.5, 133.6, 129.8, 129.4, 128.6, 128.5, 128.0, 127.8, 127.6, 127.5, 127.4, 125.9, 114.5, 114.5, 73.8, 70.1, 70.0, 65.8, 37.6, 31.2, 30.6; IR (KBr-disc) ν 3433 (w), 3033 (w), 2910 (w), 2887 (m), 2856 (w), 1610 (m), 1582 (w), 1510 (s), 1454 (m), 1383 (m), 1297 (w), 1238 (s), 1174 (s), 1112 (w), 1081 (m), 1066 (m), 1045 (m); LRMS (FAB) *m/z* 476 ([M + H]<sup>+</sup>, 13 %), 197 (11 %), 136 (65 %), 91 (55 %); HRMS (FAB) *m/z* calcd. for C<sub>33</sub>H<sub>32</sub>O<sub>3</sub> [M]<sup>+</sup>: 476.2351, found 476.2381; Anal. calcd. for C<sub>33</sub>H<sub>32</sub>O<sub>3</sub>: C, 83.2; H, 6.8; found C, 83.0; H, 6.6.

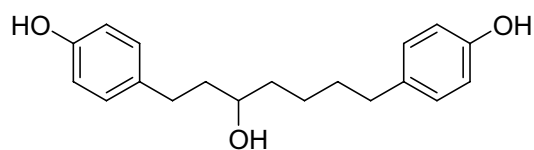
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )



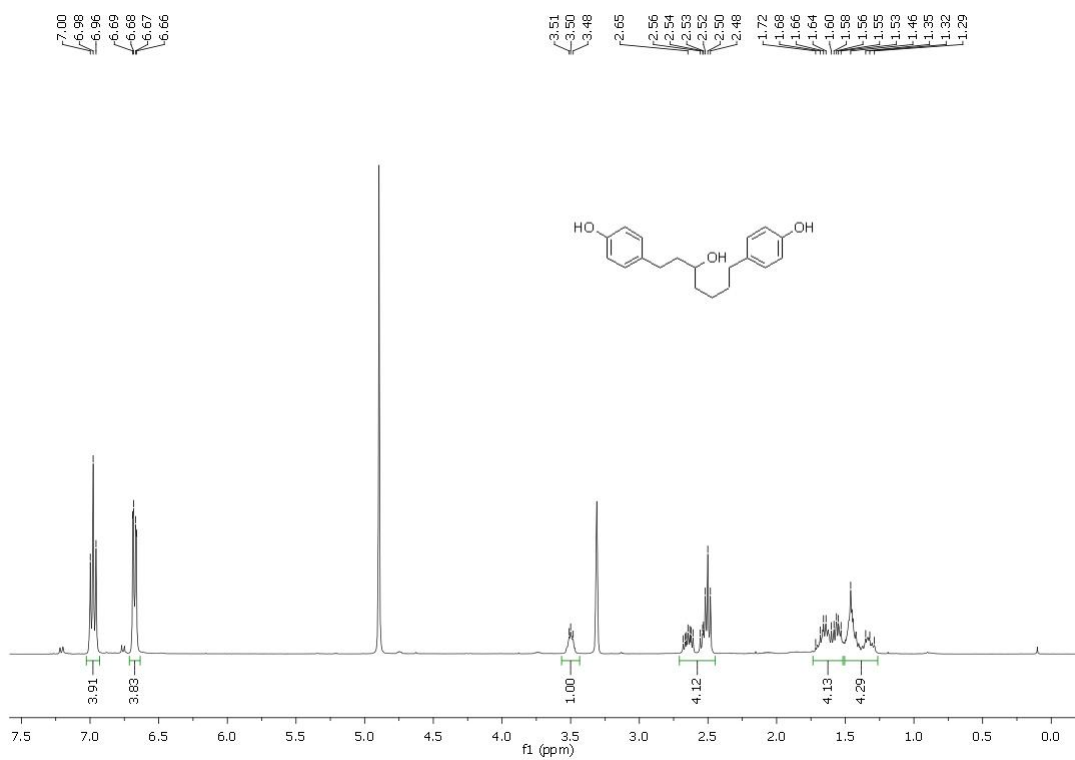
D4 *rac*-Centrololol (*rac*-III)



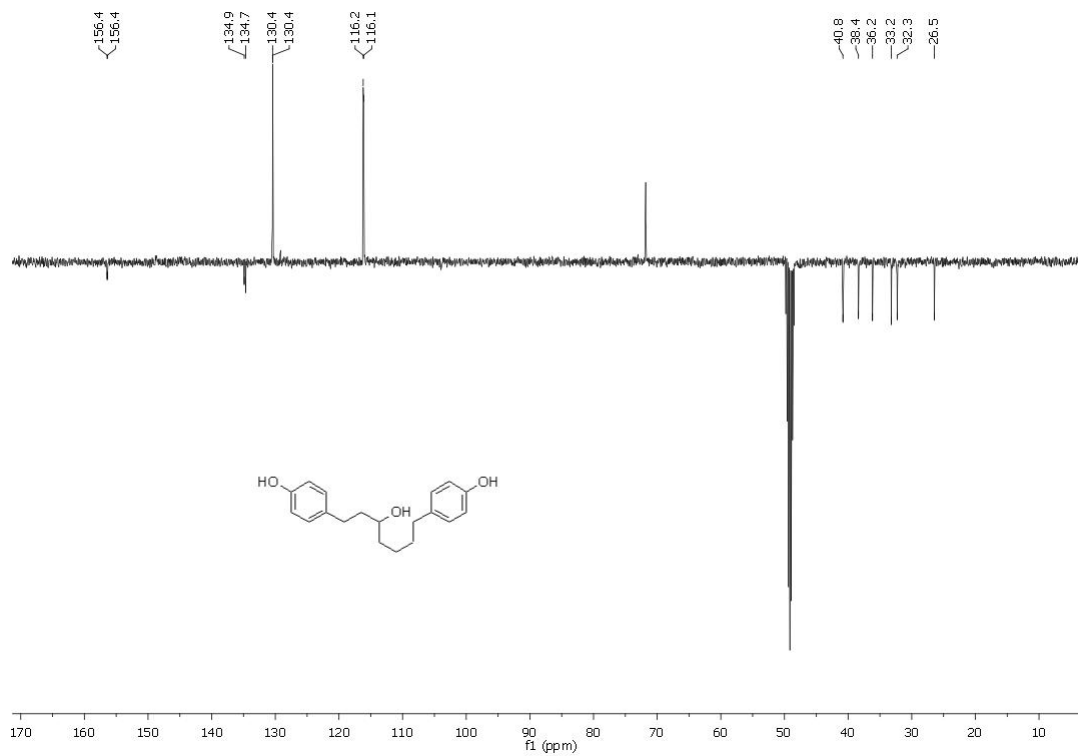
*rac*-Centrololol (*rac*-III)

*Rac*-8 (50 mg, 0.1 mmol) was dissolved in dry and degassed toluene (10 mL). Pd on charcoal (10 wt-% based on dry mass, 10 mg) was added, and the mixture was three times degassed and saturated with hydrogen, and then stirred under an atmosphere of hydrogen for 12 hours. The solvent was evaporated, and the residue was chromatographed on silica using cyclohexane/MTBE as eluent to give *rac*-centrololol (*rac*-III) in 74% (22 mg, 0.07 mmol) yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  7.00 – 6.96 (4H), 6.69 – 6.66 (4H), 3.50 (m, 1H) 2.65 (dddd,  $J = 5.5, 5.6, 9.5, 14.2, 1\text{H}$ ), 2.58 - 2.48 (3H), 1.72 – 1.53 (4H), 1.50 – 1.29 (4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  156.3, 156.3, 134.8, 134.6, 130.3, 130.3, 116.1, 116.0, 71.7, 40.7, 38.3, 36.1, 33.1, 32.2, 26.4.

### $^1\text{H}$ NMR (400 MHz, $\text{CD}_3\text{OD}$ )

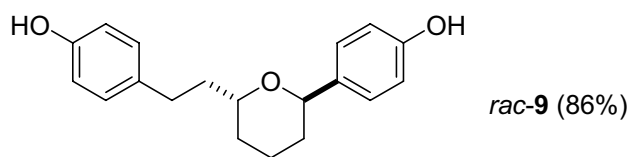


### $^{13}\text{C}$ NMR (100 MHz, $\text{CD}_3\text{OD}$ )



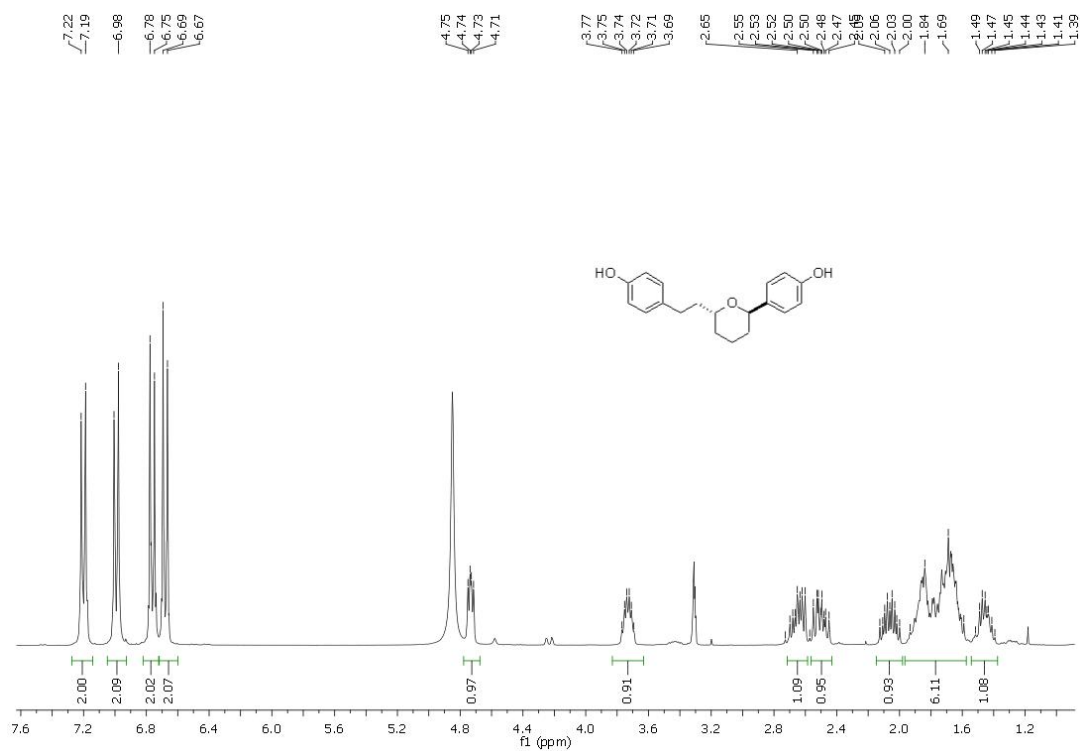


D5 *rac-epi-De-O-methyl centrolobine (rac-9)*

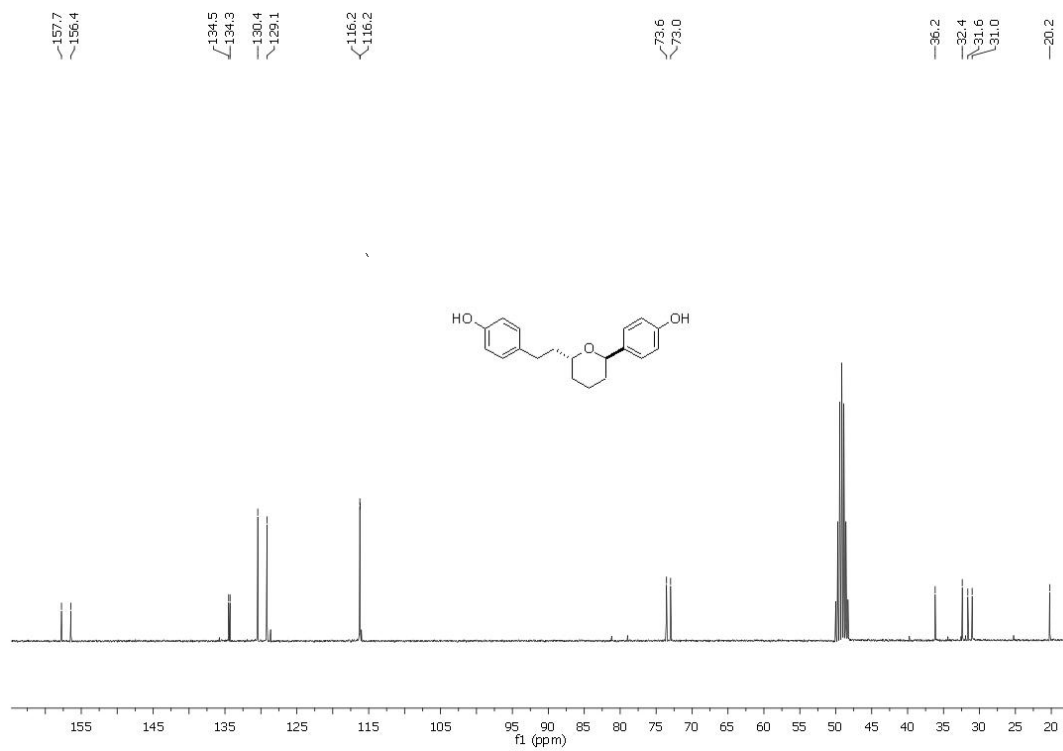


To a solution of *rac-8* (150 mg, 0.32 mmol) in methanol (20 mL) was added Pd(OH)<sub>2</sub>/C (20 wt.-% Pd based on dry mass, 9 mg). The suspension was saturated with hydrogen and kept under an atmosphere of hydrogen (1 bar) for 12 hours. The solvent was evaporated, and the residue was purified by flash chromatography on silica (hexanes-ethyl acetate 1 : 1) to give the title compound in 86% (81 mg, 0.28 mmol) yield as a colourless solid, mp 186°C. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ 7.20 (d, *J* = 8.5, 2H), 6.99 (d, *J* = 8.5, 2H), 6.76 (d, *J* = 8.6, 2H), 6.68 (d, *J* = 8.5, 2H), 4.73 (dd, *J* = 4.1, 6.6, 1H), 3.73 (ddd, *J* = 4.9, 8.9, 13.8, 1H), 2.65 (ddd, *J* = 5.5, 9.9, 14.2, 1H), 2.50 (ddd, *J* = 6.8, 9.5, 13.8, 1H), 2.06 (dddd, *J* = 5.4, 9.3, 9.7, 14.4, 1H), 1.97 – 1.57 (6H), 1.45 (m, 1H); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>OD) δ 157.8, 156.4, 134.5, 134.3, 130.4, 129.2, 116.2, 116.2, 73.6, 73.0, 36.2, 32.4, 31.6, 31.0, 20.2; IR (KBr-disc) ν 3325 (m), 2933 (m), 2856 (m), 1613 (m), 1512 (s), 1452 (m), 1240 (s), 1071 (m), 1024 (m); LRMS (ESI) *m/z* 227 (100%), 299 (42%); HRMS (ESI) *m/z* calcd. for C<sub>19</sub>H<sub>23</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 299.1647, found 299.1658; Anal. calcd. for C<sub>19</sub>H<sub>22</sub>O<sub>3</sub>: C, 76.5 %; H, 7.4 %; found C, 75.9 %, H, 7.4 %.

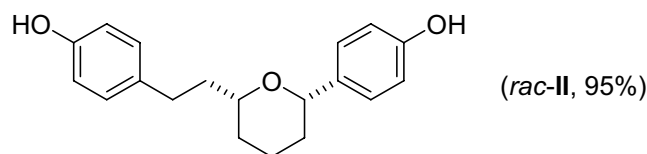
### $^1\text{H}$ NMR (300 MHz, $\text{CD}_3\text{OD}$ )



### $^{13}\text{C}$ NMR (75 MHz, $\text{CD}_3\text{OD}$ )

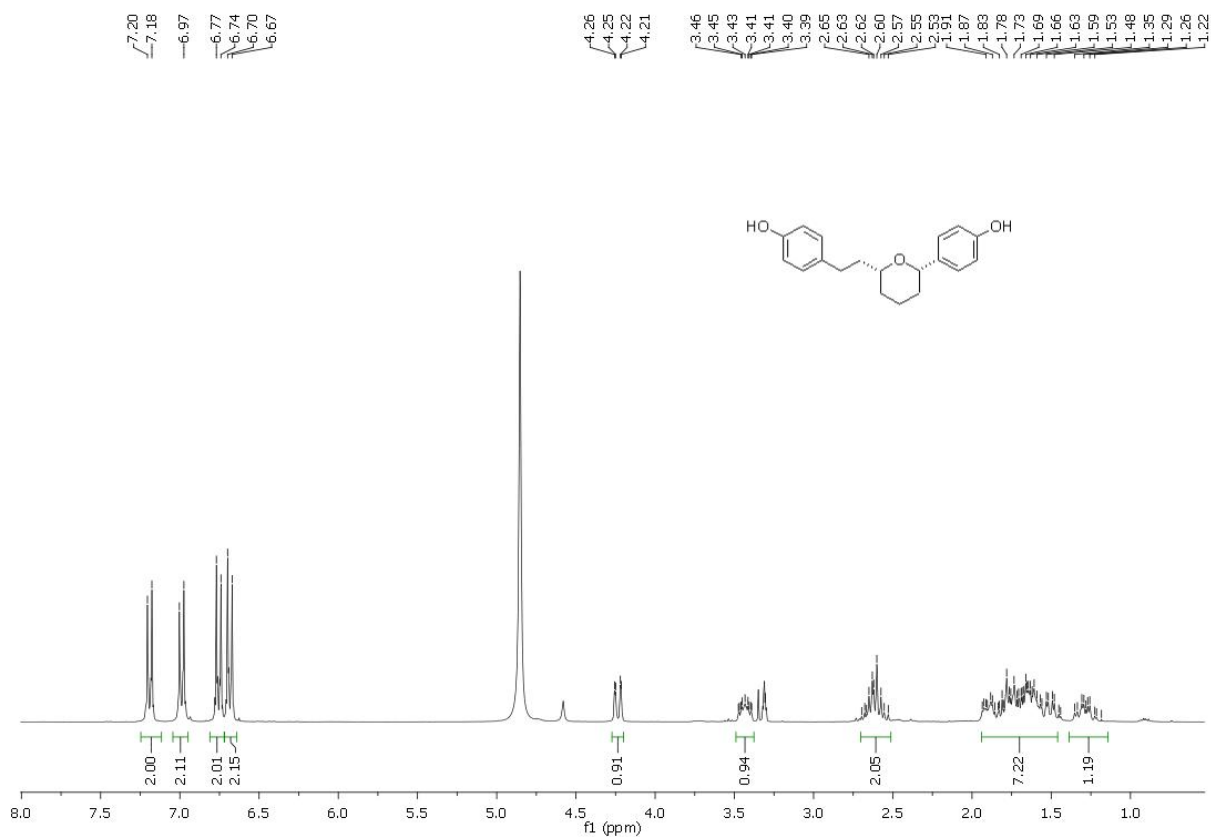


D6 *rac-de-O-Methylcentrolobine (rac-II)*



To a solution of *rac-9* 40 mg, 0.13 mmol) in methanol (1.3 mL) was added HCl (aq., 4 M, 67  $\mu$ L, 0.26 mmol). The solution was stirred for 12 hours at ambient temperature and then diluted with MTBE (10 mL). The organic layer was separated, washed with water, and the aqueous layer was extracted with MTBE. The combined organic extracts were dried with MgSO<sub>4</sub>, filtered, and all volatiles were removed in vacuo. The residue was purified by column chromatography on silica (hexanes – MTBE 1 : 1) to give *rac-de-O-methyl centrolobine (rac-II)* in 95% (38 mg, 0.12 mmol) yield, mp 162°C. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD)  $\delta$  7.19 (d,  $J$  = 8.4, 2H), 6.99 (d,  $J$  = 8.5, 2H), 6.76 (d,  $J$  = 8.6, 2H), 6.68 (d,  $J$  = 8.5, 2H), 4.23 (dd,  $J$  = 1.8, 10.9, 1H), 3.43 (m, 1H), 2.70 – 2.51 (2H), 1.94 – 1.46 (8H), 1.27 (1H); <sup>13</sup>C-NMR (75 MHz, CD<sub>3</sub>OD)  $\delta$  157.8, 156.4, 135.8, 134.6, 130.5, 128.7, 116.2, 116.0, 81.2, 79.0, 39.8, 34.4, 32.6, 31.9, 25.2; IR (KBr-disc)  $\nu$  3324 (m), 2935 (m), 2858 (m), 2360 (w), 1614 (m), 1514 (s), 1445 (m), 1228 (s), 1072 (m), 1025 (m); LRMS (ESI)  $m/z$  187 (50%), 281 (40%), 299 (100%); HRMS (ESI)  $m/z$  calcd. for C<sub>19</sub>H<sub>23</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 299.1647, found 299.1629; Anal. calcd. for C<sub>19</sub>H<sub>22</sub>O<sub>3</sub>: C, 76.5%; H, 7.4%, gefunden C, 75.9%; H 7.4%.

### $^1\text{H}$ NMR (300 MHz, $\text{CD}_3\text{OD}$ )



### $^{13}\text{C}$ NMR (75 MHz, $\text{CD}_3\text{OD}$ )

