Electrosynthesis using a recyclable mediator-electrolyte system based on ionically tagged phenyl iodide and 1,1,1,3,3,3-hexafluoroisopropanol

Supporting Information

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1. General Remarks

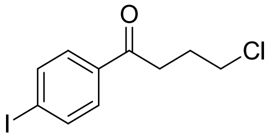
^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on an AVANCE 250, 300 or 500 spectrometer (Bruker). Chemical shifts are reported in parts per million (ppm, δ scale) referenced to the indicated signal of residual non- or partially deuterated solvent. Mass spectrometry (MS) was carried out either with electron ionization or with electrospray ionization using a MAT 95 XP (Thermo Finnigan). Novel compounds were additionally characterized with elemental analysis using a Flash EA 112 (Thermo Fisher) and with high resolution mass spectrometry using a 6210 TOF LC-MS System (Agilent). Gas chromatography was carried out using a HP 1100 (Thermo Fisher) equipped with a 30 m HP5 column. All dry solvents were purchased from Acros Organics (AcroSeal) and used as received, if not noted otherwise. 1,1,1,3,3,3-Hexafluoroisopropanol (>99% purity) and 2,2,2-trifluoroethanol (>99% purity) were purchased from Fluorochem and used as received.

Cyclic voltammetry

The experiments were carried out in a conventional three electrode cell using a Parstat 4000 (Princeton Applied Research). A glassy carbon disc (diameter: 0.16 mm) served as working electrode and a platinum wire as counter electrode. The glassy carbon disc was polished using polishing alumina (0.05 µm) prior to each experiment. As reference a Ag/AgNO$_3$ electrode (silver wire in 0.1 M NBu$_4$ClO$_4$/CH$_3$CN solution; c(AgNO$_3$) = 0.01 M; E_0 = −87 mV vs. ferrocene redox couple and +548 mV vs. NHE)[1] was used and this compartment separated from the rest of the cell with a Vycor frit. As electrolyte, 0.1 M NBu$_4$ClO$_4$ (Aldrich, Electrochemical grade) was employed in the corresponding fluorinated solvent. The electrolyte was purged with argon for at least five minutes prior to recording the CVs.

2. Synthesis of mediator salt 1

2.1 4-Chloro-1-(4-iodophenyl)butan-1-one (5)



To a suspension of aluminum trichloride (5.98 g, 44.85 mmol) in CH_2Cl_2 (20 mL) was added, under argon atmosphere, 4-chlorobutyryl chloride (6.32 g, 5.03 mL, 44.85 mmol) over a period of 15 min and the mixture was stirred at 0 °C for 90 min. To the cooled solution, iodobenzene (9.15 g, 5.00 mL, 44.85 mmol) was added dropwise over 30 min. and the solution was stirred at room temperature for 2.5 h. After pouring the reaction mixture in ice-cold water (100 mL), CH_2Cl_2 (40 mL) was added and the organic layer separated. Then it was washed with $Na_2S_2O_3$ solution (15 wt%, 2 x 20 mL), sat. K_2CO_3 (2 x 20 mL), H_2O (3 x 40 mL), and finally brine (30 mL). After drying over anhydrous Na_2SO_4, all volatiles were evaporated under reduced pressure. The crude product was used for the following step without further purification. In order to obtain an analytically pure sample, the crude product was recrystallized from *n*-heptane/diethylether and obtained as a pale green solid.

Yield: 8.28 g (26.91 mmol, 60%).

Mp.: 50 °C.

^{1}H NMR (300 MHz, acetone-*d*$_6$): δ(ppm) = 2.17 (quin, *J* = 6.8 Hz, 2H), 3.22 (t, *J* = 7.0 Hz, 2H), 3.72 (t, *J* = 6.6 Hz, 2H), 7.72 - 7.86 (m, 2H), 7.88 - 7.98 (m, 2H).

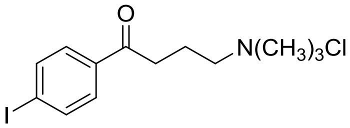
^{13}C NMR (63 MHz, acetone-*d*$_6$): δ(ppm) = 27.9, 36.1, 45.3, 101.2, 130.5, 137.4, 138.9, 198.8.

GC-MS (m/z): 308 ($[M]^+$, ^{35}Cl; 3), 246 (42), 232 (6), 231 (100), 203 (33), 181 (9), 145 (5), 127 (11), 104 (14), 77 (9), 76 (37), 75 (11), 74 (14), 51 (6), 50 (23), 49 (7), 41 (18), 39 (13).

HRMS (EI): Calc. [$C_{10}H_{10}{}^{35}ClIO$]: 307.9459, found 307.9461. Calc [$C_{10}H_{10}{}^{37}ClIO$] 309.9430, found 307.9437.

Elemental analysis: Calc. for $C_{10}H_{10}ClIO$: C 38.93, H 3.27, found C 38.86, H 3.16.

2.2 *N*-[4-(4-Iodophenyl)-4-oxobutyl]-*N*,*N*,*N*-trimethylammonium chloride (6)



4-Chloro-1-(4-iodophenyl)butan-1-one (2.00 g, 6.48 mmol) was dissolved in acetonitrile (10 mL) and trimethylamine was added as ethanolic solution (4.00 mL, 4.2 M). The mixture was reacted at 80 °C for 48 h in a thick-walled glass tube sealed with a screw-on Teflon cap. Then water (50 mL) and diethyl ether (25 mL) were added and the layers separated. The aqueous layer was extracted two times with diethylether (25 mL) and the extract concentrated under reduced pressure to yield the product as a colorless solid. *N*-[4-(4-Iodophenyl)-4-oxobutyl]-*N*,*N*,*N*-trimethylammonium chloride

Yield: 1.86 g (5.05 mmol, 78%).

Mp.: 298 °C (decomposition).

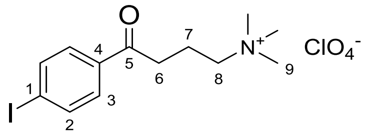
^{1}H NMR (300 MHz, water-*d*$_2$): δ(ppm) = 2.08 - 2.23 (m, 2H), 3.15 (s, 9H), 3.14 (t, *J* = 6.8 Hz, 2H), 3.37 (s, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.87 (d, *J* = 8.7 Hz, 2H).

^{13}C NMR (75 MHz, water-d$_2$): δ(ppm) = 17.0, 34.4, 52.9, 65.5, 101.7, 129.4, 135.1, 138.0, 201.4.

HRMS (ESI-TOF): Calc. m/z for $[C_{13}H_{19}INO]^+$ 332.0506, found $[C_{13}H_{19}INO]^+$ 332.0507.

Elemental analysis: Calc. [$C_{13}H_{19}ClINO$] C 42.47; H 5.21; N 3.81, found C 42.58; H 4.89; N 3.82.

2.3 *N*-[4-(4-Iodophenyl)-4-oxobutyl]-*N,N,N*-trimethylammonium perchlorate (1)



N-[4-(4-Iodophenyl)-4-oxobutyl]-*N*,*N*,*N*-trimethylammonium chloride (5.00 g, 13.60 mmol) was dissolved in water (10 mL) and an aqueous solution of sodium perchlorate monohydrate (6.80 mL, 4.0 M) is added. The precipitated solid was filtered off, washed with cold water (2 x 10 mL) and then dried in vacuum to yield **1** as a colorless solid.

Yield: 5.57 g (12.92 mmol, 95%).

Mp.: 240 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ(ppm) = 1.96 - 2.09 (m, 2H, H-7), 3.03 - 3.16 (m, 11H, H-8, H-9), 3.29 (d, *J* = 4.9 Hz, 2H, H-6), 7.65 - 7.77 (m, 2H, H-3), 7.95 (d, *J* = 8.5 Hz, 2H, H-2).

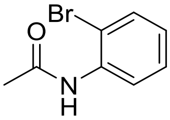
^{13}C NMR (75 MHz, DMSO-d_6): δ(ppm) = 16.8 (C-7), 34.4 (C-6), 52.2 (C-9), 64.7 (C-8), 102.0 (C-1), 129.6 (C-3), 135.6 (C-4), 137.7 (C-2), 198.1 (C-5).

HRMS (ESI-TOF): Calc. m/z for [$C_{13}H_{19}INO$]$^+$ 332.0506, found [$C_{13}H_{19}INO$]$^+$ 332.0507. Calc. [ClO_4]$^-$ 98.9490, found [ClO_4]$^-$ 98.9495.

Elemental analysis: Calc. [$C_{13}H_{19}ClINO_5$] C 36.17; H 4.44; N 3.24, found [$C_{13}H_{19}ClINO_5$] C 35.84; H 4.18; N 2.84.

3. Synthesis of the starting materials for direct oxidative C-N coupling reactions

3.1 *N*-(2-bromophenyl)acetamide[2] (7)



2-Bromoaniline (1.00 g, 5.81 mmol) was slowly added to a solution of acetic acid anhydride (2.23 g, 21.8 mmol, 2.06 mL) in dichloromethane (6 mL) at 0 °C (ice cooling) and stirred for 15 min. Then ethanol (5 mL) was added to quench the remaining anhydride. The reaction mixture was poured in a separation funnel and Et_2O (50 mL) was added. The mixture was extracted two times with 25 mL sat. aq. K_2CO_3 solution and with brine. The solvents were removed under reduced pressure and the residue dried in vacuum to yield the product as a colorless solid.

Yield: 1.23 g (5.76 mmol, 99%).

Mp.: 98 °C (Lit.: 97 - 99 °C).[2]

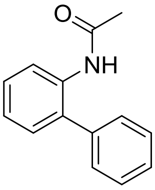
^{1}H NMR (250 MHz, chloroform-*d*): δ(ppm) = 2.23 (s, 3H), 6.97 (ddd, *J* = 7.7, 7.7, 1.6 Hz, 1H), 7.30 (ddd, *J* = 7.4, 7.4, 1.4 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.63 (br. s., 1H), 8.31 (d, *J* = 8.0 Hz, 1H).

^{13}C NMR (63 MHz, chloroform-*d*): δ(ppm) = 24.7, 113.2, 122.0, 125.1, 128.3, 132.1, 135.6, 168.2.

HRMS (EI): Calc. m/z for [$C_8H_8ON^{79}Br$]: 212.9784, found 212.9781; Calc. [$C_8H_8ON^{81}Br$]: 214.9763, found 214.9761.

Elemental analysis: Calc. [C_8H_8BrNO] C 44.80; H 3.77; N 6.54, found [C_8H_8BrNO] C 44.85; H 3.80; N 6.48.

3.2 2-Acetamidobiphenyl[3] (3a)



2-Aminobiphenyl (10.00 g, 59.09 mmol) was dissolved in Ac_2O (20 mL) and stirred for 20 minutes. The mixture was poured slowly in aq. K_2CO_3 solution (4 M, 25 mL). The precipitated solid was filtered off and washed with water until the pH value of the filtrate became neutral. After drying in vacuum, the product was obtained as a colorless solid.

Yield: 12.35 g (58.50 mmol, 98 %).

Mp.: 122 °C (Lit.: 121-122 °C).[3]

^{1}H NMR (300 MHz, chloroform-*d*): δ(ppm) = 1.92 (s, 3H), 7.06 – 7.15 (m, 2H), 7.22 – 7.46 (m, 6H), 8.16 (d, *J* = 8.0 Hz, 1H).

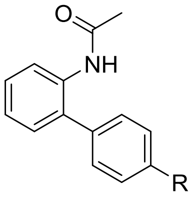
^{13}C NMR (63 MHz, chloroform-*d*): δ(ppm) = 24.5, 121.7, 124.3, 127.9, 128.3, 129.0, 129.2, 130.0, 132.2, 134.6, 138.1, 168.2.

GC-MS (m/z): 211 ([M]$^+$, 35), 170 (12), 169 (100), 168 (81), 167 (52), 166 (16), 139 (13), 43 (25).

HRMS (EI): Calc. m/z for [$C_{14}H_{13}ON$]: 211.0992, found 211.0997.

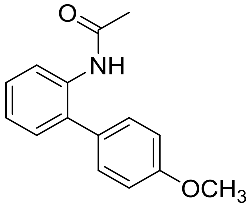
Elemental analysis: Calc. [$C_{14}H_{13}NO$] C 79.59; H 6.20; N 6.63, found [$C_{14}H_{13}NO$] C 79.32; H 6.24; N 6.49.

3.2 General procedure I for the synthesis of different 2-acetamidobiphenyls (3b-3e)



To a solution of 2-bromoaniline (1 equiv, 0.20 g, 0.94 mmol) in acetonitrile (4.79 mL) and H_2O (0.50 mL) was added the corresponding boronic acid (1.5 equiv 0.21 g, 1.40 mmol), K_2CO_3 (1.5 equiv, 0.19 g, 1.40 mmol) and $Pd(PPh_3)_4$ (0.05 g, 0.05 mmol). The mixture was heated to 80°C in a thick-walled glass tube sealed with a screw-on Tefon cap and stirred for 5 h. Then the mixture was cooled to room temperature and Et_2O (50 mL) was added. The organic layer was washed three times with H_2O (3 x 25 mL) and finally with brine (10 mL). After drying over Na_2SO_4 and removal of the solvent under reduced pressure, the residue was purified using column chromatography (eluent mixture: *n*-heptane/ethyl acetate, gradient from 4:1 to 1:2).

3.4 2-Acetamido-4'-methoxybiphenyl[4] (3b)



A solution of 2-bromoaniline (1 equiv, 0.20 g, 0.94 mmol) in acetonitrile (5 mL) and water (0.5 mL) was converted according to general procedure I with 4-methoxyphenylboronic acid (1.5 equiv, 0.21 g, 1.40 mmol), K_2CO_3 (1.5 equiv, 0.19 g, 1.40 mmol) and $Pd(PPh_3)_4$ (0.05 g, 0.05 mmol). After purification **3b** was obtained as a colorless solid.

Yield: 0.23 g (0.93 mmol, 99%).

Mp.: 135 °C (Lit.: 134 °C).[4]

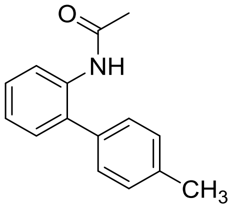
^1H NMR (300 MHz, chloroform-*d*): δ(ppm) = 2.03 (s, 3H), 3.87 (s, 3H), 6.95 – 7.06 (m, 2H), 7.11 – 7.39 (m, 6H), 8.25 (d, *J* = 8.1 Hz, 1H).

^{13}C NMR (75 MHz, chloroform-*d*): δ(ppm) = 24.5, 55.3, 114.4, 121.5, 124.2, 128.0, 130.1, 130.2, 130.3, 131.8, 134.8, 159.3, 168.2.

GC-MS (m/z): 241 ($[M]^+$, 59), 200 (14), 199 (100), 198 (14), 184 (32), 167 (12), 154 (27), 128 (14), 127 (11), 43 (23).

HRMS (EI): Calc. m/z for $[C_{15}H_{15}O_2N]$: 241.1097, found 241.1098.

3.5 2-Acetamido-4'-methylbiphenyl[5] (3c)



A solution of 2-bromoaniline (1 equiv, 0.20 g, 0.94 mmol) in acetonitrile (5 mL) and water (0.5 mL) was converted according to general procedure I with *p*-tolylboronic acid (1.5 equiv 0.19 g, 1.40 mmol),

K_2CO_3 (1.5 equiv, 0.19 g, 1.40 mmol) and $Pd(PPh_3)_4$ (0.05 g, 0.05 mmol). After purification, **3c** was obtained as a colorless solid.

Yield: 0.20 g (0.87 mmol, 93%).

Mp.: 105 °C (Lit.: 105 °C).[5]

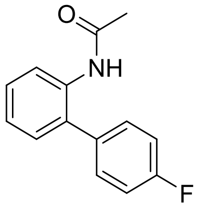
^1H NMR (300 MHz, chloroform-*d*): δ(ppm) = 2.00 (s, 3H), 2.42 (s, 3H), 7.07 - 7.42 (m, 8H), 8.23 (d, *J* = 8.1 Hz, 1H).

^{13}C NMR (75 MHz, chloroform-*d*): δ(ppm) = 24.5, 55.3, 114.4, 121.5, 124.2, 128.0, 130.1, 130.2, 130.3, 131.8, 134.8, 159.3, 168.2.

GC-MS (m/z): 225 ([M]$^+$, 46), 184 (14), 183 (100), 182 (52), 181 (12), 180 (27), 168 (25), 167 (41), 152 (10), 43 (25).

HRMS (EI): Calc. m/z for [$C_{15}H_{15}ON$]: 225.1148, found 225.1147.

3.6 2-Acetamido-4'-fluorobiphenyl[5] (3d)



A solution of 2-bromoaniline (1 equiv, 0.20 g, 0.94 mmol) in acetonitrile (5 mL) and water (0.5 mL) was converted according to general procedure I with 4-fluorophenylboronic acid (1.5 equiv 0.20 g, 1.40 mmol), K_2CO_3 (1.5 equiv, 0.19 g, 1.40 mmol) and $Pd(PPh_3)_4$ (0.05 g, 0.05 mmol). After purification, **3d** was obtained as a colorless solid.

Yield: 0.17 g (0.76 mmol, 81%).

Mp.: 124 °C (Lit.: 125 °C).[5]

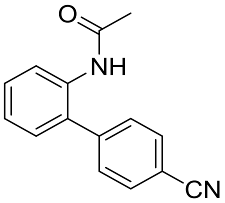
^1H NMR (300 MHz, chloroform-*d*): δ(ppm) = 2.01 (s, 3H), 7.03 - 7.26 (m, 5H), 7.29 - 7.43 (m, 3H), 8.16 (d, *J* = 8.1 Hz, 1H).

^{13}C NMR (75 MHz, chloroform-*d*): δ(ppm) = 24.3, 115.9 (d, *J* = 21.5 Hz, 2C), 122.3, 124.6, 128.4, 130.0, 130.8 (d, *J* = 7.7 Hz, 2C), 131.7, 134.1 (d, *J* = 3.3 Hz, 1C), 134.6, 162.2 (d, *J* = 247.6 Hz, 1C), 168.3.

GC-MS (m/z): 229 ([M]$^+$, 33), 188 (13), 187 (100), 186 (54), 185 (37), 184 (11), 43 (23).

HRMS (EI): Calc. m/z for [$C_{14}H_{12}ONF$]: 229.0897, found 229.0897.

3.7 2-*N*-Acetamido-4'-cyanobiphenyl[6] (8)



A solution of 2-bromoaniline (1 equiv, 0.20 g, 0.94 mmol) in acetonitrile (5 mL) and water (0.5 mL) was converted according to general procedure I with 4-cyanophenylboronic acid (1.5 equiv 0.21 g, 1.40 mmol), K_2CO_3 (1.5 equiv, 0.19 g, 1.40 mmol) and $Pd(PPh_3)_4$ (0.05 g, 0.05 mmol). After purification, **8** was obtained as a colorless solid.

Yield: 0.21 g (0.91 mmol, 99%).

Mp.: 165 °C (Lit.: 165 °C).[6]

^{1}H NMR (250 MHz, chloroform-d): δ(ppm) = 1.96 (s, 3H), 6.93 (br. s., 1H), 7.17 (d, *J* = 3.6 Hz, 2H), 7.29 - 7.40 (m, 1H), 7.40 - 7.49 (m, 2H), 7.57 - 7.75 (m, 2H), 7.99 (d, *J* = 8.0 Hz, 1H).

^{13}C NMR (63 MHz, chloroform-*d*): δ(ppm) = 24.2, 111.7, 118.4, 123.6, 125.3, 129.4, 129.9, 130.0, 131.7, 132.6, 134.2, 143.4, 168.4.

GC-MS (m/z): 236([M]$^{+}$, 20), 195 (15), 194 (100), 192 (38), 43 (30).

HRMS (EI): Calc. [$C_{15}H_{12}ON_2$]: 236.0944, found 236.0944.

4. Direct oxidative C-N coupling reactions with electrochemically generated species 2b

4.1 General procedure II for the electrolysis of 1

1 (0.86 g, 2.00 mmol) was dissolved in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) (10 mL) in an undivided electrolysis cell. A glassy carbon plate (immersed surface: A = 1 cm^2) was used as anode and a platinum sheet as cathode. Molecular sieve 4 Å (200 mg) was added and the solution purged with argon for 1 min. Then the solution is electrolyzed in the dark with a current density of 15 mA cm^{-2} until 1 F per mol mediator **1** are passed. For the subsequent reaction, the mixture is used as a 67 mM solution of compound **2b** (corresponds to the Faradaic efficiency of 67% under optimized conditions, see Table S1 - Table S3).

2b is stable in solution but not in its isolated form (for more details see section 9). NMR characterization was therefore carried out by analysis of the electrolyte solution containing **1** and **2b** (diluted with $CDCl_3$).

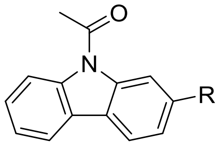
^{1}H NMR (300 MHz, chloroform-d): δ(ppm) = 2.09 - 2.27,* 3.12,* 3.20 - 3.27,* 3.32,* 4.28 (spt, J = 5.9 Hz, 2H), 8.04 - 8.11 (m, 2H), 8.18 - 8.25 (m, 2H).

^{19}F NMR (282 MHz, chloroform-d): δ(ppm) = −75.22.

^{13}C NMR (75 MHz, chloroform-d): δ(ppm) = 16.7,** 34.0,** 66.0,** 128.9,** 130.5, 133.7, 138.4,** 198.8.

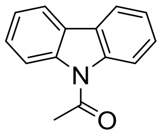
*^{1}H NMR signals of species **1** and **2b** are overlapping and not resolved. **^{13}C NMR signals of species **1** and **2b** are overlapping with resolved peaks.

4.2 General procedure III for synthesis of different *N*-acetylcarbazoles (4a-4d)



To the electrochemically prepared solution of **2b** (2.0 equiv, 0.34 mmol, see general procedure II) in HFIP, one equivalent **3** (0.17 mmol) is added. After completed reaction (monitoring with TLC), HFIP is distilled off at reduced pressure and room temperature. The remaining solid is dissolved in acetonitrile (25 mL). Then Et_2O (50ml) is added to precipitate **1** which is filtered off. After washing the solid with ethyl acetate (25 mL), **1** is analytically pure and can be reused for further electrolyses. The ethereal reaction mixture is washed three times with water (3 x 15 mL) and with brine (10 mL) and then dried over anhydrous Na_2SO_4. After removal of all volatiles under reduced pressure, the crude product was purified using flash chromatography (eluent mixture: ethyl acetate/heptanes, gradient 9:1 – 4:1 vol:vol).

4.3 *N*-Acetylcarbazole[7] (4a)



2b (2.0 equiv, 0.34 mmol, preparation according to general procedure II) in HFIP is reacted with one equivalent **3a** (35.2 mg, 0.17 mmol) following general procedure III. Purification yields **4a** as a colorless solid.

Yield: 31 mg (0.15 mmol, 89%).

Mp.: 71 °C (Lit.: 69-71 °C).[7]

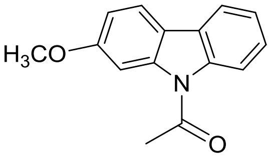
^{1}H NMR (300 MHz, chloroform-*d*): δ(ppm) = 2.85 (s, 3H), 7.38 (ddd, *J* = 7.4, 1.1 Hz, 2H), 7.48 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 2H), 7.94 - 8.00 (m, 2H), 8.20 (d, *J* = 8.3 Hz, 2H).

^{13}C NMR (75 MHz, chloroform-*d*): δ(ppm) = 27.6, 116.1, 119.7, 123.6, 126.3, 127.2, 138.5, 170.0.

GC-MS (m/z): 209 ([M]$^{+}$, 22), 168 (14), 167 (100), 166 (22), 140 (14), 139 (13), 43 (12).

HRMS (EI): Calc. [$C_{14}H_{11}ON$]: 209.0835, found 209.0832.

4.4 2-Methoxy-*N*-acetylcarbazole[5] (4b)



2b (2.0 equiv, 0.34 mmol, preparation according to general procedure II) in HFIP is reacted with one equivalent **3b** (40.2 mg, 0.17 mmol) following general procedure III. Purification yields **4b** as a colorless solid.

Yield: 26 mg (0.11 mmol, 66%).

Mp.: 80 °C (Lit.: 82 °C).[5]

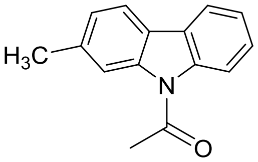
^{1}H NMR (300 MHz, chloroform-*d*): δ(ppm) = 2.88 (s, 3H), 3.94 (s, 3H), 7.00 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.41 (ddd, *J* = 7.4, 7.4, 1.7 Hz), 7.36 (ddd, *J* = 7.4, 7.4, 1.1 Hz), 7.80 - 7.97 (m, 3H), 8.03 - 8.09 (m, 1H).

^{13}C NMR (75 MHz, chloroform-*d*): δ(ppm) = 27.7, 55.8, 102.0, 111.4, 115.7, 119.2, 119.7, 120.2, 123.7, 125.9, 126.7, 138.4, 140.1, 159.8, 170.2.

GC-MS (m/z): 239 ([M]$^{+}$, 68), 198 (14), 197 (100), 196 (16), 182 (66), 154 (58), 153 (44), 128 (11), 127 (20), 126 (14), 43 (32).

HRMS (EI): Calc. [$C_{15}H_{13}O_{2}N$]: 239.0941, found 239.0937.

4.5 2-Methyl-*N*-acetylcarbazole[5] (4c)



2b (2.0 equiv, 0.34 mmol, preparation according to general procedure II) in HFIP is reacted with one equivalent **3c** (37.6 mg, 0.17 mmol) following general procedure III. Purification yields **4c** as a colorless solid.

Yield: 31 mg (0.14 mmol, 84%).

Mp.: 85 °C (Lit.: 87 °C).[5]

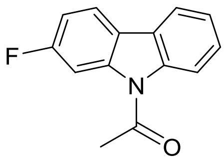
^{1}H NMR (300 MHz, chloroform-*d*): δ(ppm) = 2.56 (s, 3H), 2.88 (s, 3H), 7.22 (dq, *J* = 7.9, 0.6 Hz, 1H), 7.34 - 7.41 (m, 1H), 7.42 - 7.49 (m, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.93 - 7.99 (m, 1H), 8.06 (s, 1H), 8.17 (d, *J* = 8.3 Hz, 1H).

^{13}C NMR (75 MHz, chloroform-*d*): δ(ppm) = 22.3, 27.7, 116.1, 116.7, 119.4, 119.5, 123.6, 124.0, 124.9, 126.6, 126.7, 137.6, 138.6, 139.0, 170.1.

GC-MS (m/z): 223 ([M]$^{+}$, 33), 182 (14), 181 (100), 180 (82), 179 (12), 178 (12), 152 (20), 43 (19).

HRMS (EI): Calc. [$C_{15}H_{13}ON$]: 223.0992, found 223.0987.

4.6 2-Fluoro-*N*-acetylcarbazole[5] (4d)



2b (2.0 equiv, 0.34 mmol, preparation according to general procedure II) in HFIP is reacted with one equivalent **3d** (35.6 mg, 0.17 mmol) following general procedure III. Purification yields **4d** as a colorless solid.

Yield: 36 mg (0.16 mmol, 94%).

Mp.: 102 °C (Lit.: 101-102 °C).[5]

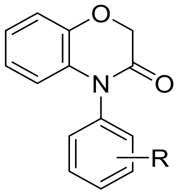
^{1}H NMR (300 MHz, chloroform-*d*): δ(ppm) = 2.88 (s, 3H), 7.14 (ddd, *J* = 8.6, 8.6, 2.4 Hz, 1H), 7.40 (ddd, *J* = 7.4, 0.8 Hz, 1H), 7.47 (ddd, *J* = 8.1, 7.4, 1.5 Hz, 1H), 7.88 - 7.98 (m, 2H), 8.05 - 8.13 (m, 2H).

^{13}C NMR (75 MHz, chloroform-*d*): δ(ppm) = 27.6 (s), 104.5 (d, *J* = 29.7 Hz), 111.5 (d, *J* = 23.7 Hz), 115.8 (s), 119.7 (s), 120.4 (d, *J* = 9.9 Hz), 122.4 (s), 123.8 (s), 126.0 (s), 126.8 (s), 138.8 (s), 139.3 (d, *J* = 12.1 Hz), 162.4 (d, *J* = 243.7 Hz), 169.9 (s).

GC-MS (m/z): 227 ([M]$^+$, 20), 186 (14), 185 (100), 184 (23), 158 (12), 157 (11), 43 (15).

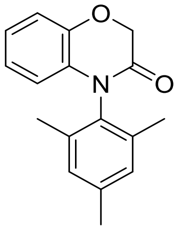
HRMS (EI): Calc. [$C_{14}H_{10}ONF$]: 227.0741, found 227.0739.

4.7 General procedure IV for synthesis of different *N*-arenylamides (4e-4j)



To the electrochemically prepared solution of **2b** (2.0 equiv, 0.66 mmol, see general procedure II) in HFIP, one equivalent of the corresponding amide (0.33 mmol) and aryl (10.0 equiv 3.33 mmol; in the case of iodoarenes and naphtalene: 2.0 equiv, 0.67 mmol) are added. After completed reaction (monitoring with TLC), HFIP is distilled off at reduced pressure at room temperature. The resulting solid is dissolved in acetonitrile (25 mL). Then Et_2O (50 ml) is added to precipitate **1** which is filtered off. After washing the solid with ethyl acetate (25 mL), **1** is obtained in analytical purity and can be reused for further electrolyses. The product mixture is washed three times with water (3 x 15 mL) and with brine (10 mL) and then dried over anhydrous Na_2SO_4. After removal of all volatiles under reduced pressure, the crude product is purified using flash chromatography (eluent mixture: ethyl acetate/heptanes, gradient 9:1 – 4:1 vol:vol).

4.8 4-Mesityl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one[8] (4e)



2b (2.0 equiv, 0.66 mmol, preparation according to general procedure II) in HFIP is reacted with one equivalent 2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (49.2 mg, 0.33 mmol) and mesitylene (0.40 g, 0.45 mL, 3.33 mmol, addition via Hamilton syringe) following general procedure IV. Purification yields **4e** as a colorless solid.

Yield: 70 mg (0.26 mmol, 79%).

Mp.: 162 °C.

^{1}H NMR (300 MHz, chloroform-*d*): δ(ppm) 2.07 (s, 6H), 2.36 (s, 3H), 4.80 (s, 2H), 6.30 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.81 - 6.89 (m, 1H), 6.96 - 7.10 (m, 4H).

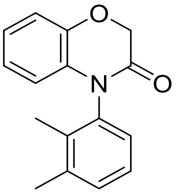
^{13}C NMR (75 MHz, chloroform-*d*): δ(ppm) = 17.4, 21.1, 67.9, 115.6, 116.9, 122.8, 124.0, 128.9, 129.7, 130.6, 136.1, 138.9, 144.9, 163.4.

GC-MS (m/z): 267 ([M]$^+$, 100), 238 (24), 224 (26), 210 (18), 209 (10), 208 (36), 196 (12), 181 (13), 180 (12), 120 (17), 119 (40), 117 (10), 115 (12), 103 (10), 91 (28), 77 (20), 65 (13).

HRMS (EI): Calc. [$C_{17}H_{17}O_2N$]: 267.1254, found 267.1252.

Elemental analysis: Calc. [$C_{17}H_{17}NO_2$] C 76.38; H 6.41; N 5.24, found [$C_{17}H_{17}NO_2$] C 76.74; H 6.36; N 5.15.

4.9 4-(2,3-Dimethylphenyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one[8] (4f)



2b (2.0 equiv, 0.66 mmol, preparation according to general procedure I) in HFIP is reacted with one equivalent 2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (49.2 mg, 0.33 mmol) and *o*-xylene (0.35 g, 0.40 mL, 3.33 mmol, addition via Hamilton syringe) following general procedure IV. Purification yields **4f** as a colorless solid and 7.9 mg of the starting material.

Yield: 56 mg (0.22 mmol, 67%, 84% based on recovered starting material).

Mp.: 132 °C.

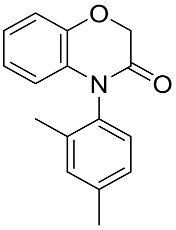
^{1}H NMR (300 MHz, dichloromethane-*d*$_2$): δ(ppm) = 2.31 (s, 3H), 2.34 (s, 3H), 4.73 (s, 2H), 6.44 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.84 (ddd, *J* = 8.0, 7.2, 1.8 Hz, 1H), 6.93 - 7.06 (m, 4H), 7.30 (d, *J* = 7.7 Hz, 1H).

^{13}C NMR (75 MHz, dichloromethane-*d*$_2$): δ(ppm) = 19.6, 19.9, 68.6, 117.0, 117.2, 122.7, 124.1, 126.3, 129.9, 131.2, 131.3, 133.9, 138.0, 139.1, 145.3, 164.5.

GC-MS (m/z): 253 ([M]$^+$, 74), 225 (17), 224 (100), 196 (21), 120 (11), 103 (11), 79 (10), 77 (21), 65 (11), 63 (10).

HRMS (EI): Calc. [$C_{16}H_{15}O_2N$]: 253.1097, found 253.1099.

4.10 4-(2,4-Dimethylphenyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one[8] (4g)



2b (2.0 equiv, 0.66 mmol, preparation according to general procedure I) in HFIP is reacted with one equivalent 2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (49.2 mg, 0.33 mmol) and *m*-xylene (0.35 g, 0.40 mL, 3.33 mmol, addition via Hamilton syringe) following general procedure IV. Purification yields **4g** as a colorless solid and 7.9 mg of the starting material.

Yield: 60 mg (0.24 mmol, 73%).

Mp.: 137 °C.

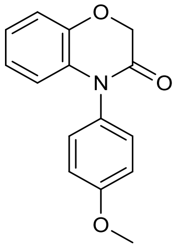
^{1}H NMR (300 MHz, dichloromethane-d_2): δ(ppm) = 2.09 (s, 3H), 2.40 (s, 3H), 4.75 - 4.82 (m, 2H), 6.34 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.85 (ddd, *J* = 7.2, 7.2, 1.7 Hz, 1H), 6.99 (ddd, *J* = 7.9, 7.9, 1.5 Hz, 1H), 7.04 - 7.11 (m, 2H), 7.14 - 7.24 (m, 2H).

^{13}C NMR (75 MHz, dichloromethane-d_2): δ(ppm) = 17.3, 21.2, 68.0, 116.3, 116.9, 122.6, 124.0, 128.3, 128.7, 129.9, 131.8, 132.3, 136.2, 139.3, 144.7, 163.9.

GC-MS (m/z): 253 ([M]$^+$, 100), 224 (52), 210 (19), 196 (18), 194 (25), 167 (15), 105 (19), 103 (15), 91 (14), 90 (10), 79 (18), 78 (16), 77 (36), 65 (17), 63 (16), 51 (17), 42 (16), 39 (13).

HRMS (EI): Calc. m/z for $[C_{16}H_{15}NO_2]^+$ 254.1176, found $[C_{16}H_{15}NO_2]^+$ 254.1180.

4.11 4-(4-Methoxyphenyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one[9] (4h)



2b (2.0 equiv, 0.34 mmol, preparation according to general procedure I) in HFIP is reacted with one equivalent 2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (25 mg, 0.166 mmol) and anisole (10 equiv, 180 mg, 1.66 mmol, addition via Hamilton syringe) following general procedure IV. Purification yields **4h** as an orange solid. The ^{1}H and ^{13}C NMR spectroscopical data is in agreement with literature data.

Yield: 10 mg (0.04 mmol, 24%).

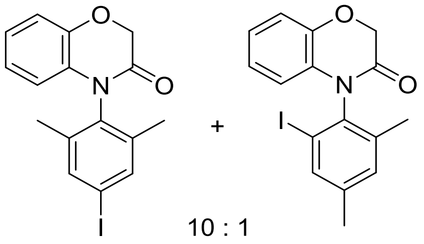
Mp.: 124 °C.

^{1}H NMR (300 MHz, dichloromethane-d_2): δ(ppm) = 3.87 (s, 3H), 4.78 (s, 2H), 6.48 (dd, *J* = 8.0, 1.4 Hz, 1 H), 6.82 - 6.91 (m, 1H), 6.96 - 7.09 (m, 4H), 7.17 - 7.25 (m, 2H).

^{13}C NMR (75 MHz, dichloromethane-d_2): δ(ppm) = 55.5, 68.1, 115.2, 116.8, 116.9, 122.5, 123.9, 128.1, 129.7, 130.8, 144.8, 159.6, 164.5.

GC-MS (m/z): 257 (13), 256 ([M]$^+$, 94), 226 (100), 212 (14), 182 (22), 63 (11).

4.12 4-(4-Iodo-2,6-dimethylphenyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (4i) and 4-(2-iodo-4,6-dimethylphenyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (4j) (10:1)



2b (2.0 equiv, 0.33 mmol, preparation according to general procedure II) in HFIP is reacted with one equivalent 2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (25 mg, 0.17 mmol) and 4-iodo-2,6-dimethylbenzene (0.385 g, 0.24 mL, 1.67 mmol, addition via Hamilton syringe) following general procedure IV.

Purification yields **4h/4i** as a yellowish solid (due to similar R_F values in various solvent mixtures, the two regioisomers could not be separated from each other).

Combined yield: 47 mg (0.12 mmol, 75%).

^{1}H NMR (250 MHz, chloroform-*d*) **4h**: δ(ppm) = 1.98 (s, 6H), 4.70 (s, 2H), 6.19 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.79 (ddd, *J* = 8.0, 7.2, 1.8 Hz, 1H), 6.89 - 6.98 (m, 1H), 6.98 - 7.04 (m, 1H), 7.51 (s, 2H); **4i**: δ(ppm) = 2.06 (s, 3H), 2.28 (s, 3H), 4.72 (s, 2H), 6.20 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.80 (ddd, *J* = 8.0, 7.2, 1.8 Hz, 1H), 6.89 - 6.98 (m, 1H), 6.98 - 7.04 (m, 1H), 7.08 (s, 1H), 7.59 (s, 1H).

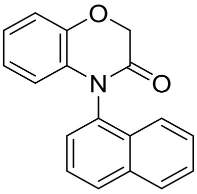
^{13}C NMR (63 MHz, chloroform-*d*) **4h**: δ(ppm) = 17.2 (2C), 67.9, 95.2, 115.3, 117.2, 123.0, 124.4, 128.4, 133.4, 137.9, 139.0, 144.8, 163.2.

GC-MS (m/z): 379 ([M]$^+$, 100), 350 (11), 231 (14), 103 (10), 77 (10).

HRMS (EI): Calc. [$C_{16}H_{14}O_2NI$]: 379.0064, found 379.0057.

Elemental analysis: Calc. [$C_{16}H_{14}O_2N$] C 50.68; H 3.72; N 3.69, found [$C_{16}H_{14}O_2N$] C 50.45; H 3.99; N 3.39.

4.13 4-(naphthalen-1-yl)-2H-benzo[b][1,4]oxazin-3(4H) (4j)



2b (2.0 equiv, 0.66 mmol, preparation according to general procedure I) in HFIP is reacted with one equivalent 2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (49.2 mg, 0.33 mmol) and naphthalene (84.5 mg, 0.66 mmol) following general procedure IV. Purification yields **4j** as an off-white solid. Our ^{1}H and ^{13}C NMR spectroscopical data is in agreement with literature data.[10]

Yield: 50 mg (0.18 mmol, 54%).

Mp.: 146 °C.

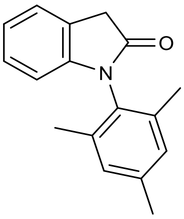
^{1}H NMR (300 MHz, chloroform-*d*): δ(ppm) = 4.85 - 4.92 (m, 1H), 4.93 - 5.00 (m, 1H), 6.25 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.77 (ddd, *J* = 7.7, 7.4, 1.5 Hz, 1H), 7.00 (ddd, *J* = 7.7, 7.4, 1.4 Hz, 1H), 7.12 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.44 - 7.58 (m, 3H), 7.60 - 7.67 (m, 2H), 7.93 - 8.05 (m, 2H).

^{13}C NMR (75 MHz, chloroform-*d*): δ(ppm) = 68.3, 116.8, 117.0, 122.3, 122.8, 124.1, 125.9, 126.7, 127.4, 127.4, 128.7, 129.7, 130.0, 130.6, 132.1, 134.8, 144.7, 164.6.

GC-MS (m/z): 275 ([M]$^+$, 100), 247 (20), 246 (100), 216 (14), 204 (24), 141 (10), 128 (41), 127 (43), 126 (24), 119 (25), 101 (10), 77 (15), 65 (10), 63 (18), 51 (14), 42 (14).

HRMS (EI): Calc. m/z for [$C_{18}H_{14}NO_2$]$^+$ 276.1019, found [$C_{18}H_{14}NO_2$]$^+$ 276.1019.

4.14 1-Mesitylindolin-2-one (4k)



2b (2.0 equiv, 0.66 mmol, preparation according to general procedure I) in HFIP is reacted with one equivalent indolin-2-one (44.4 mg, 0.33 mmol) and mesitylene (0.40 g, 0.45 mL, 3.33 mmol, addition via Hamilton syringe) following general procedure IV. Purification yields **4k** as a colorless solid and 7.9 mg of the starting material.

Yield: 35 mg (0.14 mmol, 42%).

Mp.: 105 °C.

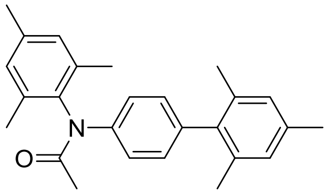
^{1}H NMR (300 MHz, chloroform-*d*): δ(ppm) = 2.09 (s, 6 H), 2.35 (s, 3 H), 3.75 (s, 2 H), 6.36 (dd, *J* = 7.7, 0.4 Hz, 1 H), 6.94 - 7.10 (m, 3 H), 7.13 - 7.22 (m, 1 H), 7.33 (dd, *J* = 7.2, 0.6 Hz, 1 H).

^{13}C NMR (75 MHz, chloroform-*d*): δ(ppm) = 17.7, 21.1, 35.9, 109.1, 122.5, 124.6, 124.6, 128.0, 129.4, 129.5, 136.4, 138.9, 144.8, 174.3.

GC-MS (m/z): GC-MS (m/z): 251 ([M]$^+$, 77), 222 (24), 209 (17), 208 (100), 206 (10), 194 (12), 193 (18), 192 (12), 119 (17), 91 (12), 89 (15), 77 (15).

HRMS (EI): Calc. m/z for [$C_{17}H_{17}NO$]$^+$ 252.1383, found [$C_{17}H_{17}NO$]$^+$ 252.1385.

4.15 *N*-mesityl-*N*-(2',4',6'-trimethyl-[1,1'-biphenyl]-4-yl)acetamide[11] (4l)



To the electrochemically generated solution of **2b** (4.0 equiv, 1.34 mmol, prepared according to general procedure II) in HFIP, acetanilide (22.5 mg, 0.16 mmol) and mesitylene (10.0 equiv, 0.20 g, 0.23 mL) are added. After completed reaction (monitoring with TLC), HFIP is distilled off at reduced pressure at room temperature. The resulting solid is dissolved in 50 mL acetonitrile. Then Et_2O (50ml) is added to precipitate **1** which is filtered off. The solid is washed with ethyl acetate (25 mL) and can be reused for further electrolyses. The ethereal mixture is washed three times with water (3 x 15 mL) and with brine (10 mL) and then dried over anhydrous Na_2SO_4. After removal of all volatiles under reduced pressure, the crude product was purified using flash chromatography (eluent mixture: ethyl acetate/heptanes, gradient 9:1 – 4:1 vol/vol and **4l** was obtained as a colorless solid.

Yield: 43 mg (0.12 mmol, 75%).

Mp.: 114 °C.

^{1}H NMR (300 MHz, chloroform-*d*): δ(ppm) = 1.9 (s, 3H), 2.0 (s, 6H), 2.2 (s, 6H), 2.3 (s, 3H), 2.4 (s, 3H), 6.9 (s, 2H), 7.0 - 7.0 (m, 3H), 7.1 (s, 1H), 7.3 (s, 1H), 7.4 (s, 1H).

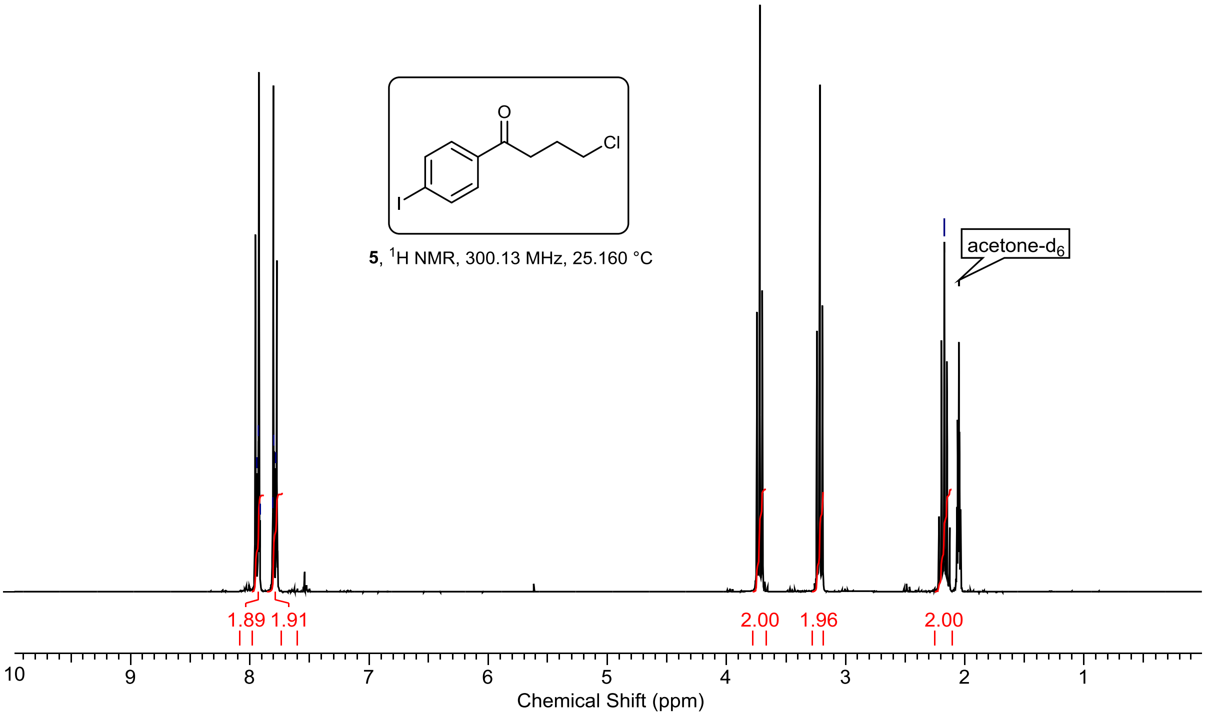
^{13}C NMR (75 MHz, chloroform-*d*): δ(ppm) = 18.0, 20.7, 21.0, 21.0, 23.9, 123.0, 128.0, 129.3, 130.0, 136.2, 136.3, 136.5, 137.2, 138.1, 138.3, 138.5, 139.3, 170.6.

GC-MS (m/z): 371 ([M]$^+$, 64), 330 (15), 329 (61), 328 (16), 313 (15), 312 (37), 237 (19), 236 (100), 208 (10), 160 (13), 43 (27).

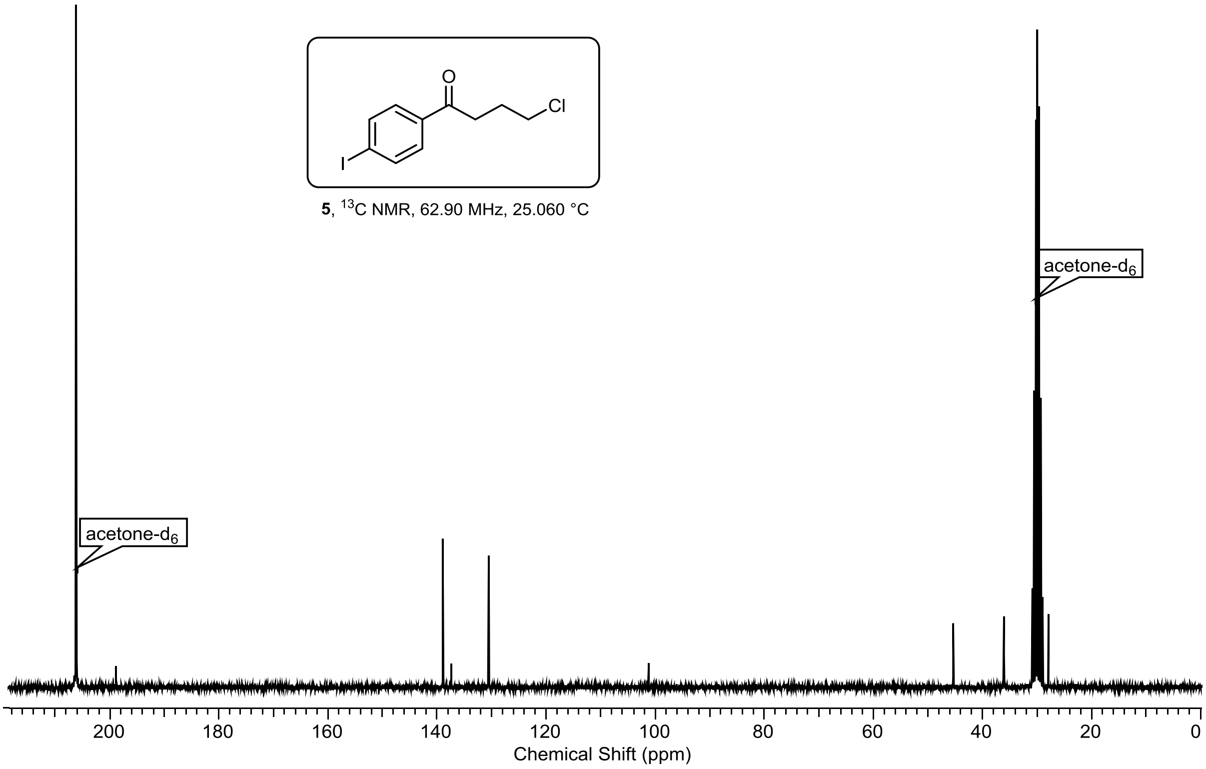
HRMS (EI): Calc. [$C_{26}H_{29}ON$]: 371.2244, found 371.2239.

5. NMR Spectra

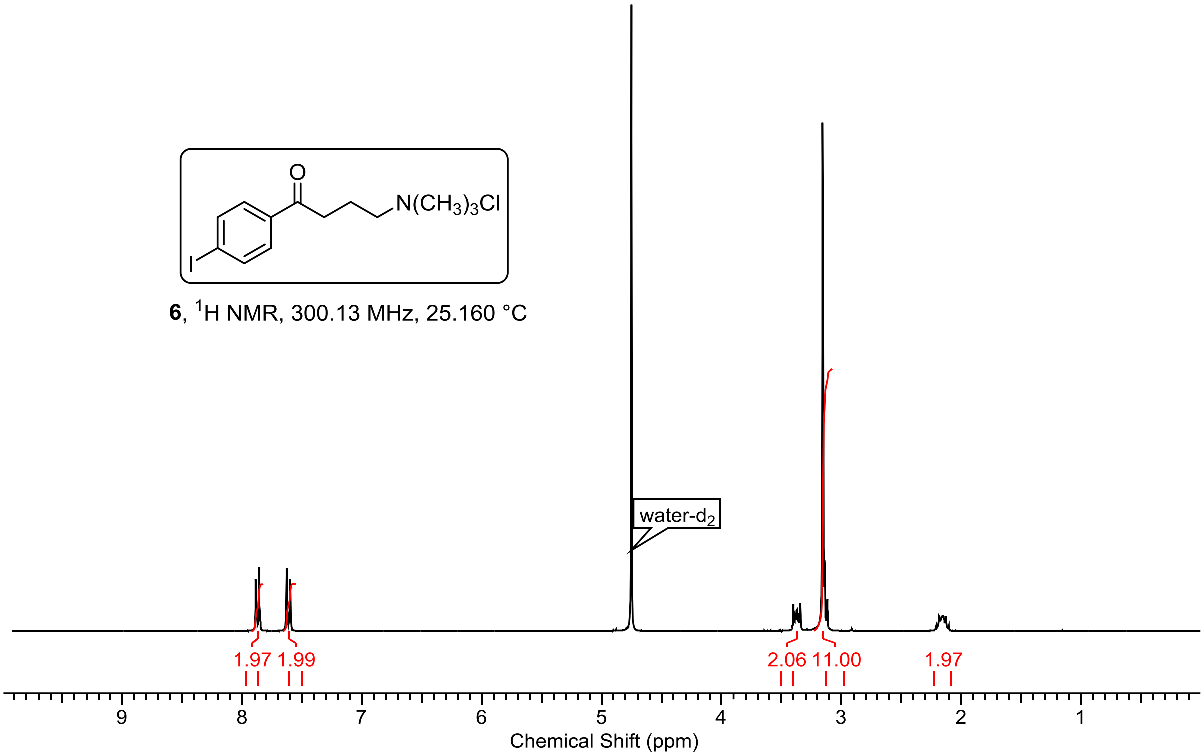
5.1 Synthesis of mediator 1



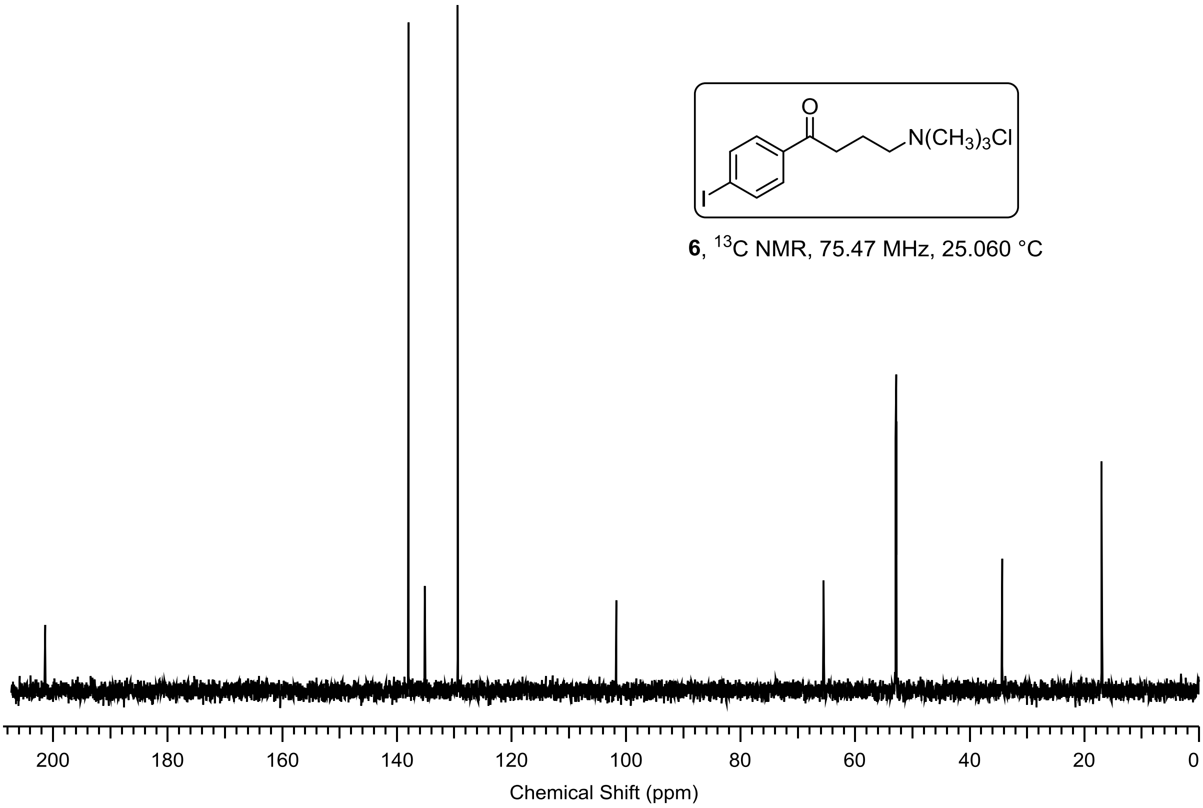
5, ^{1}H NMR, 300.13 MHz, 25.160 °C



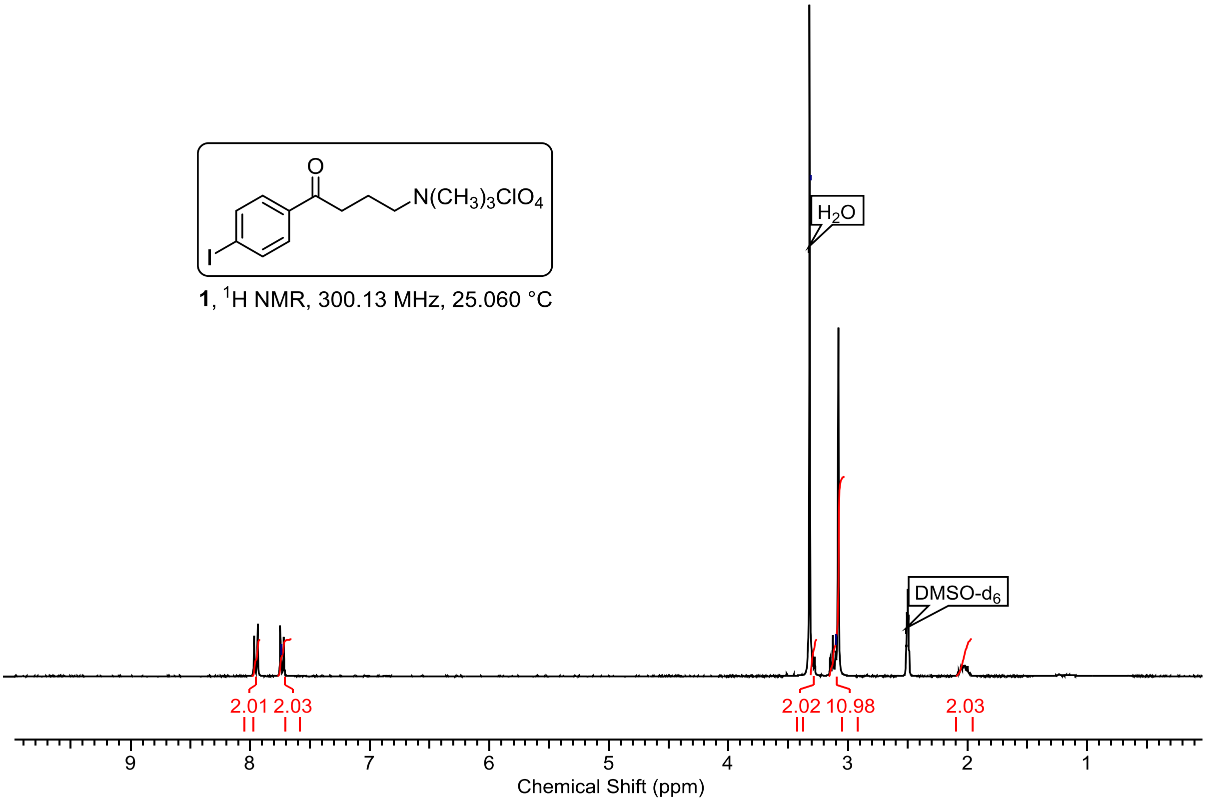
5, ^{13}C NMR, 62.90 MHz, 25.060 °C



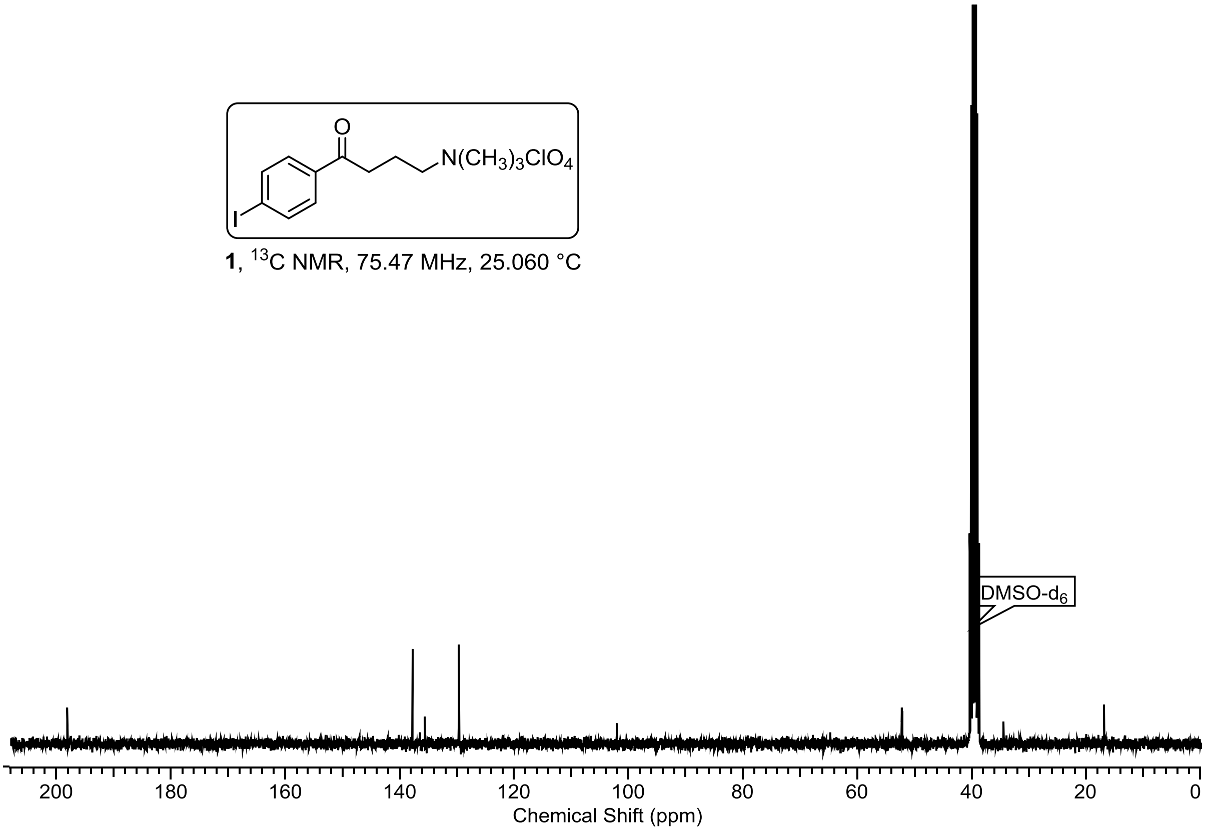
6, ^{1}H NMR, 300.13 MHz, 25.160 °C



6, ^{13}C NMR, 75.47 MHz, 25.060 °C

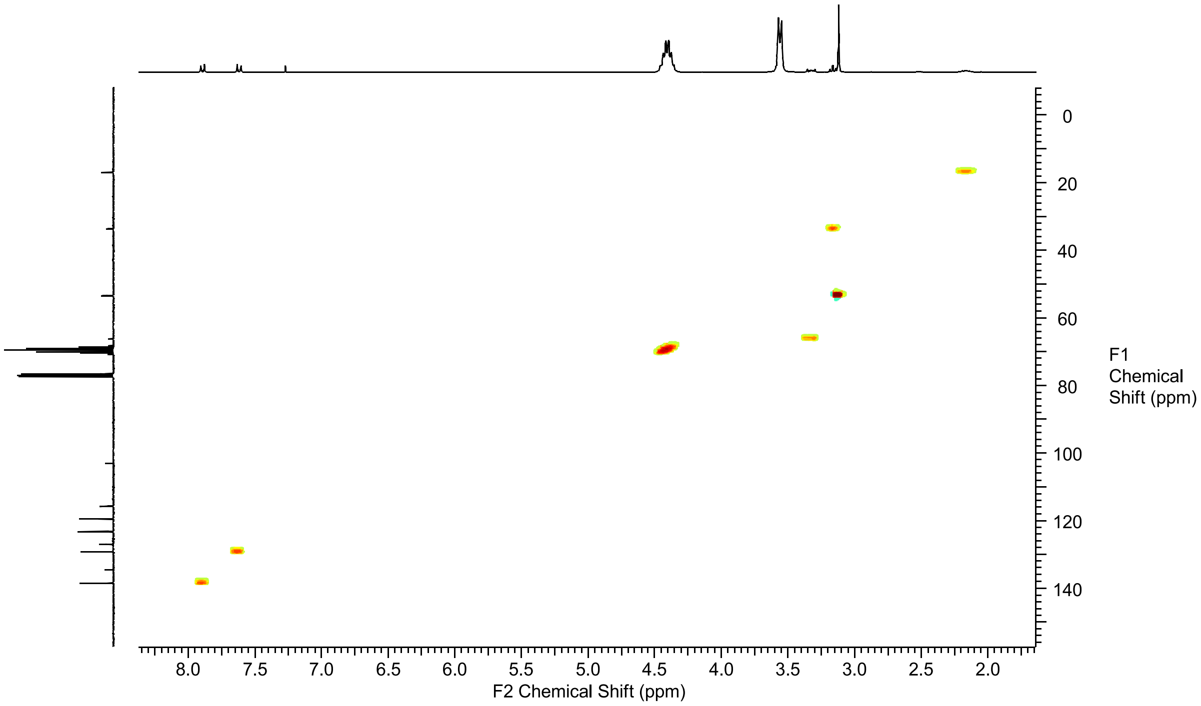


1, ^{1}H NMR, 300.13 MHz, 25.060 °C

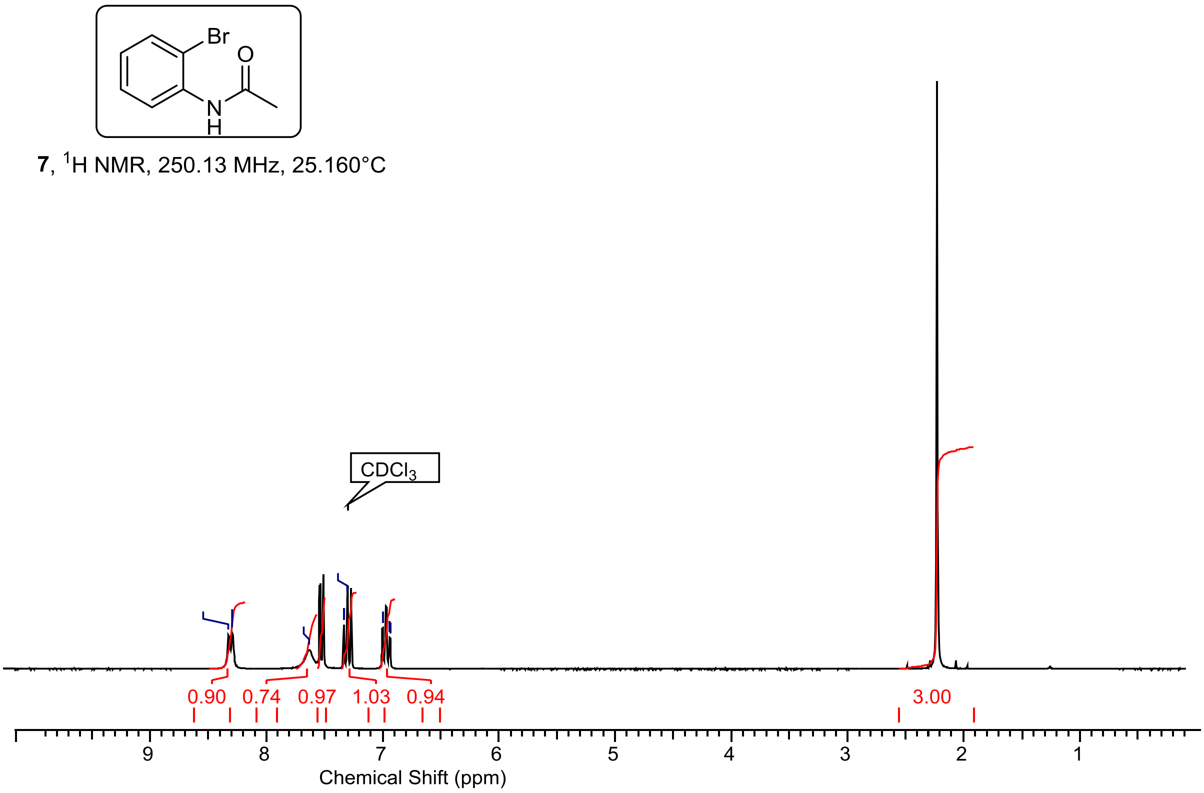


1, ^{13}C NMR, 75.47 MHz, 25.060 °C

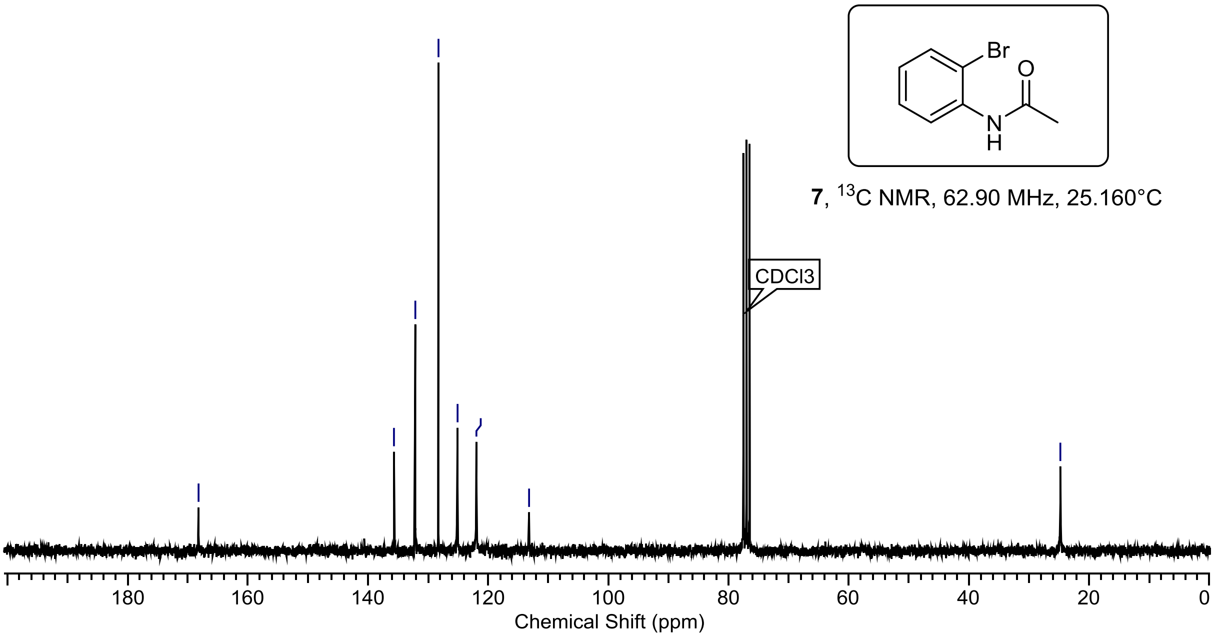
1, HSQC(^{1}H,^{13}C), 300.13 MHz, 75.47 MHz, chloroform-d, 25.360°C



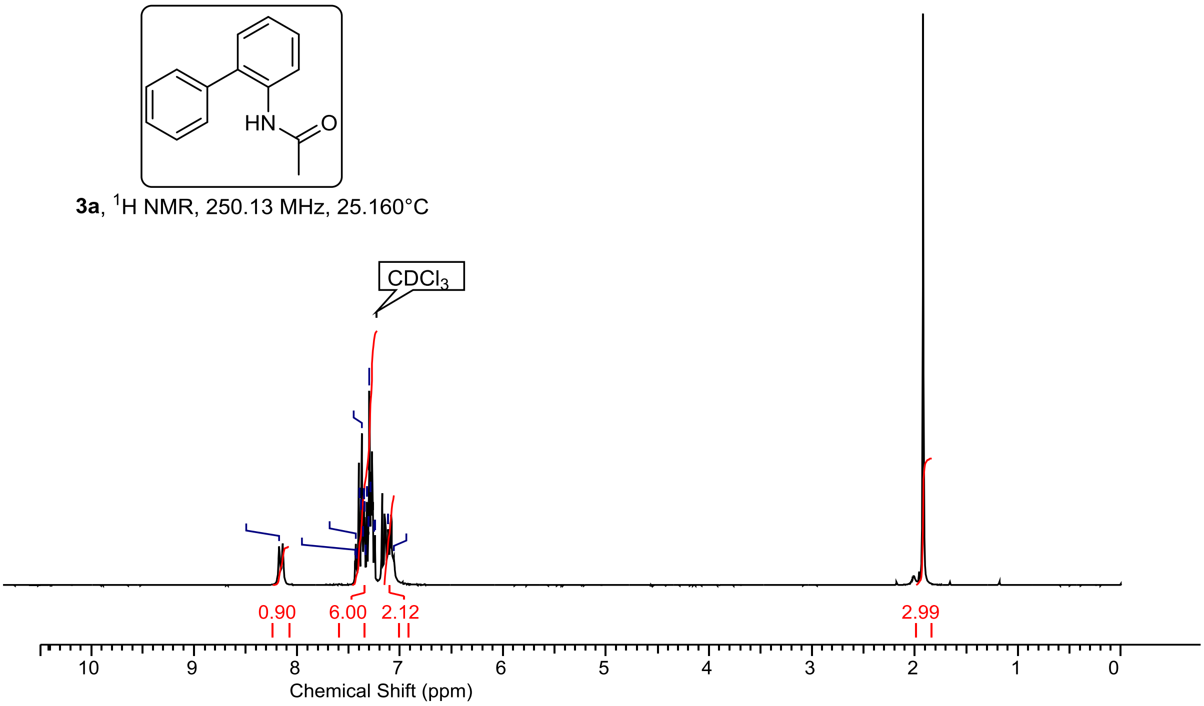
5.2 Synthesis of starting materials for oxidative C-N coupling reactions



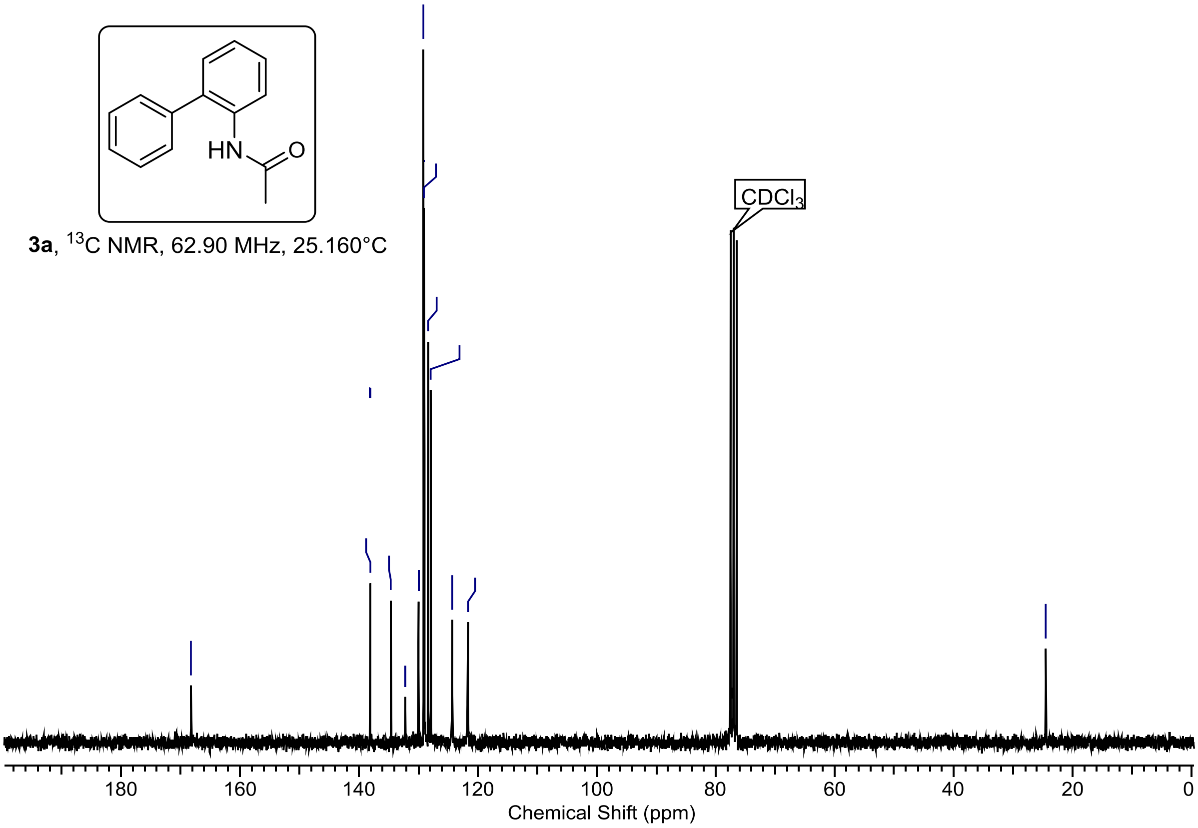
7, ^{1}H NMR, 250.13 MHz, 25.160°C



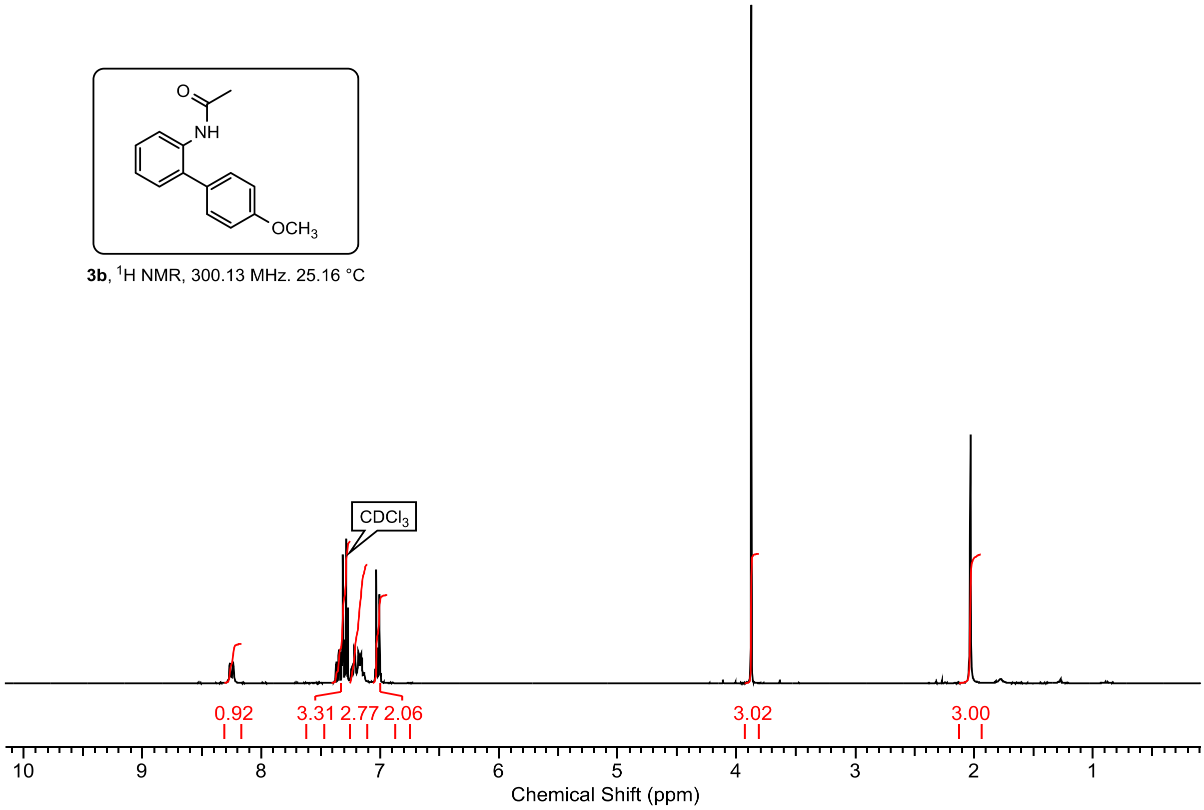
7, ^{13}C NMR, 62.90 MHz, 25.160°C



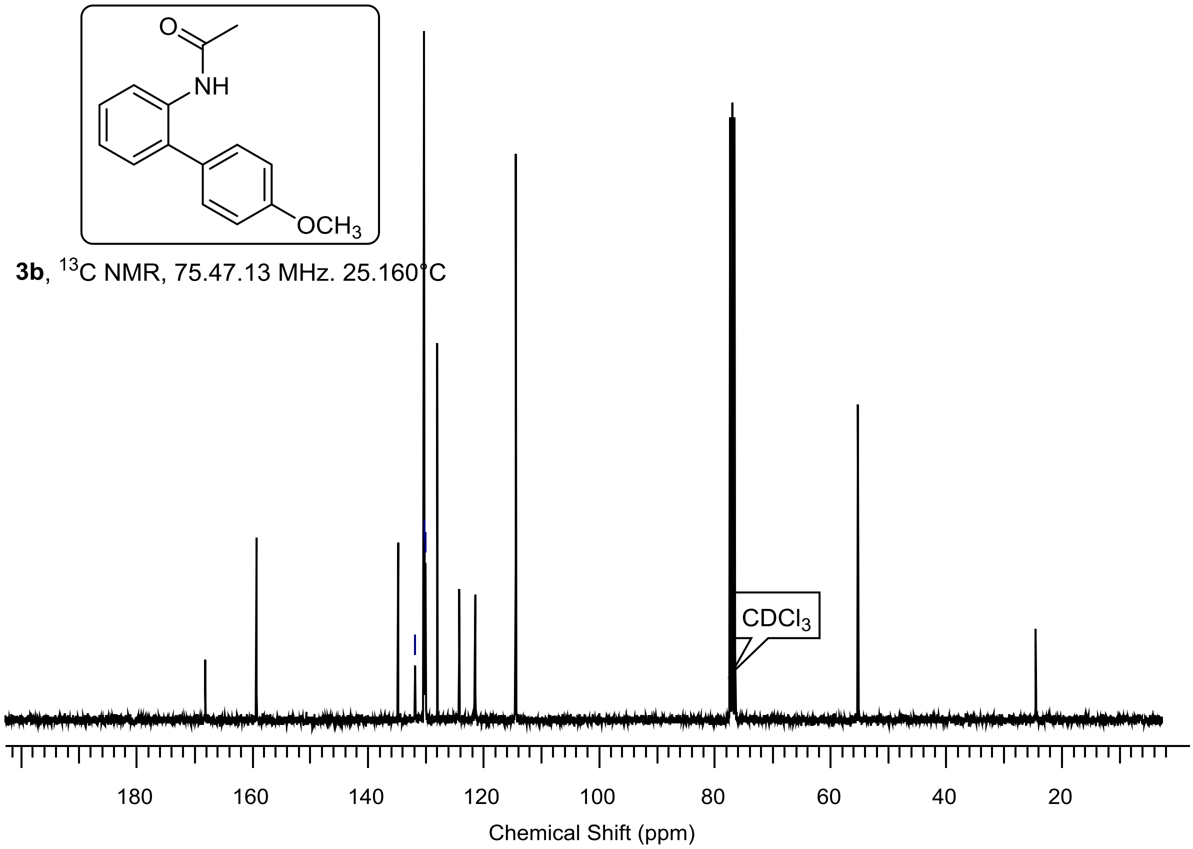
3a, ^{1}H NMR, 250.13 MHz, 25.160°C



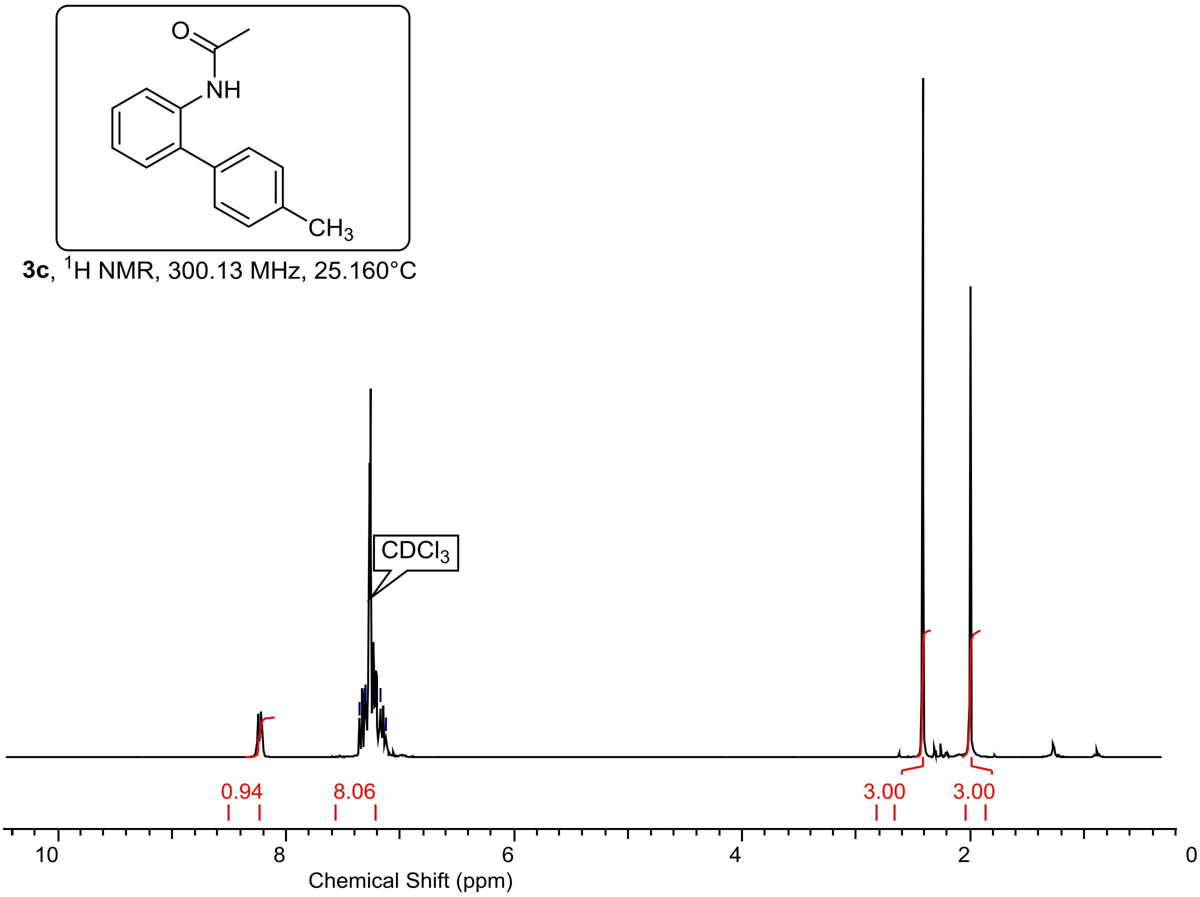
3a, ^{13}C NMR, 62.90 MHz, 25.160°C



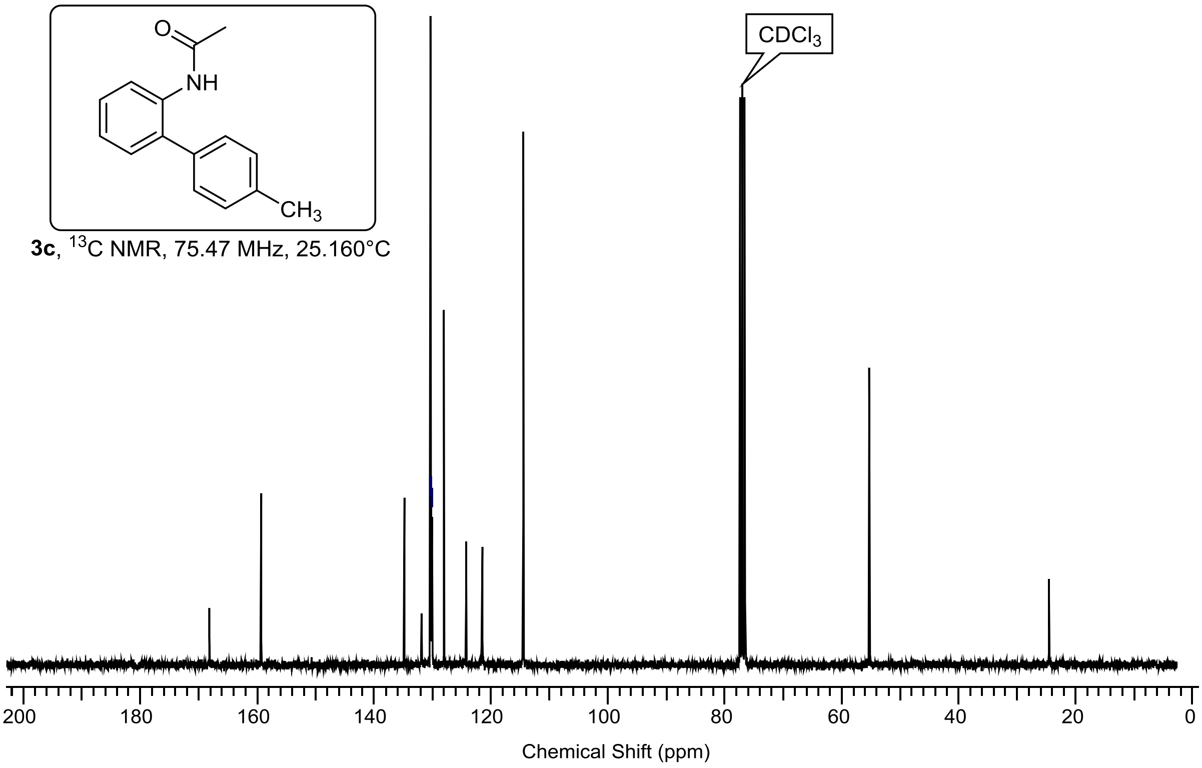
3b, ^{1}H NMR, 300.13 MHz. 25.16 °C



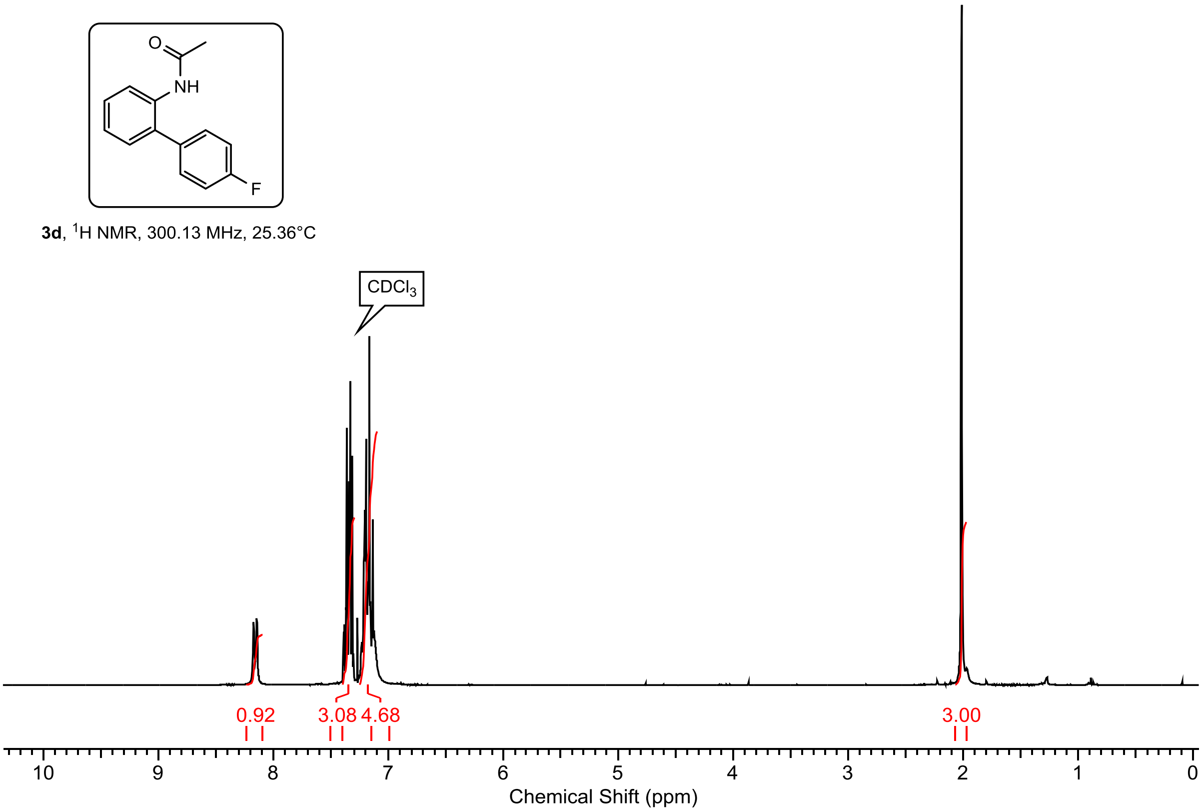
3b, ^{13}C NMR, 75.47.13 MHz. 25.160°C



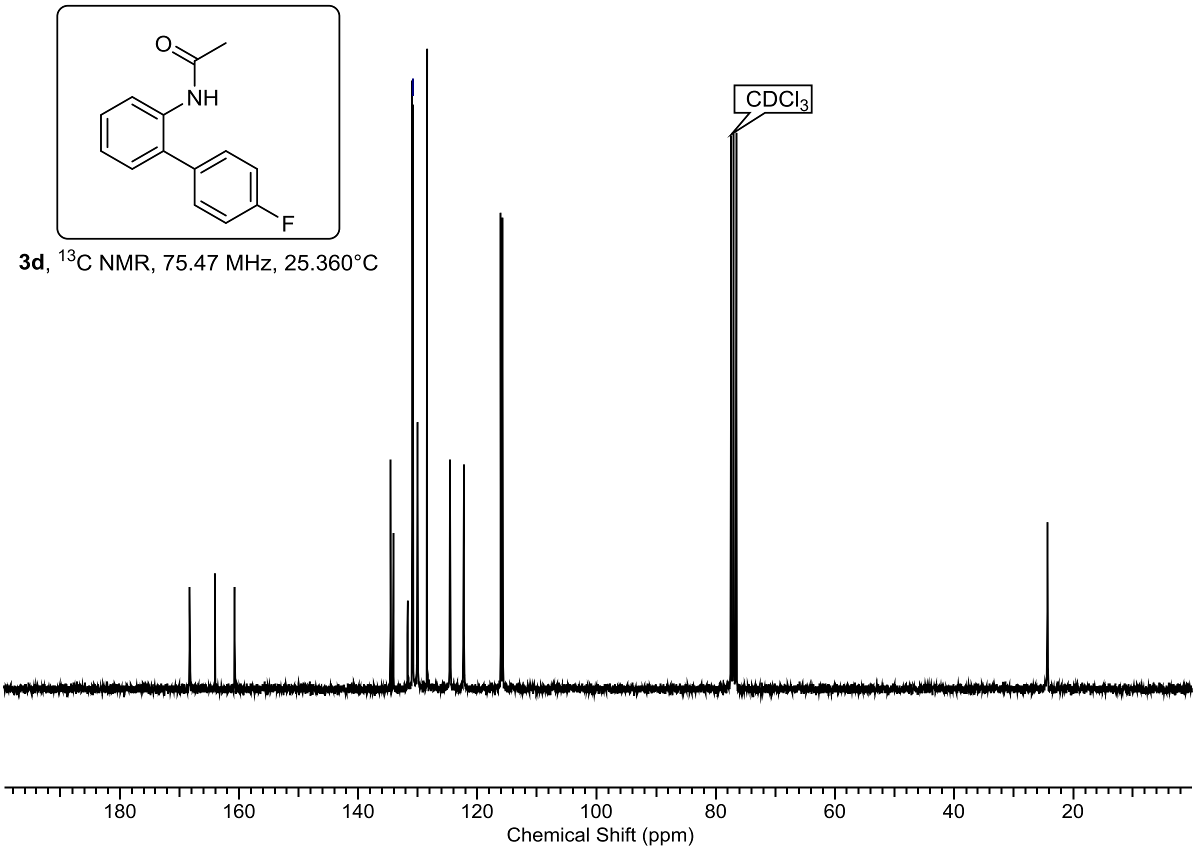
3c, ^{1}H NMR, 300.13 MHz, 25.160°C



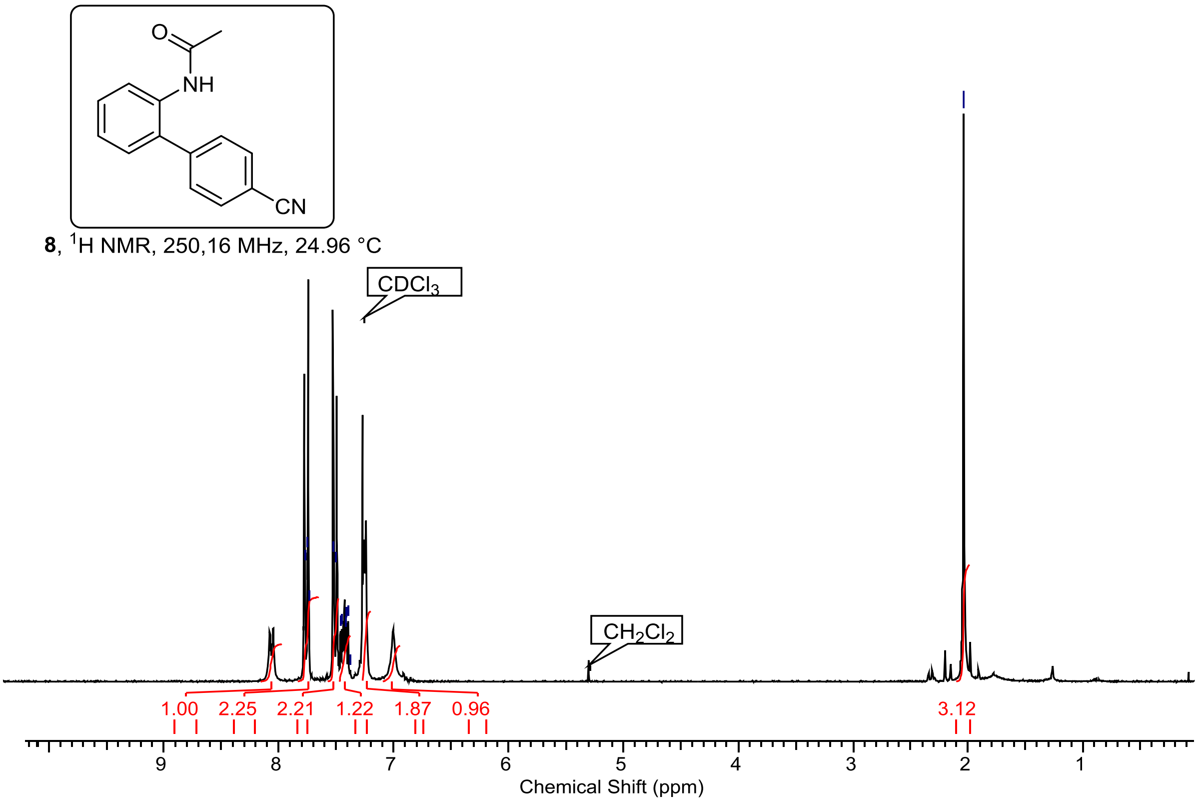
3c, ^{13}C NMR, 75.47 MHz, 25.160°C



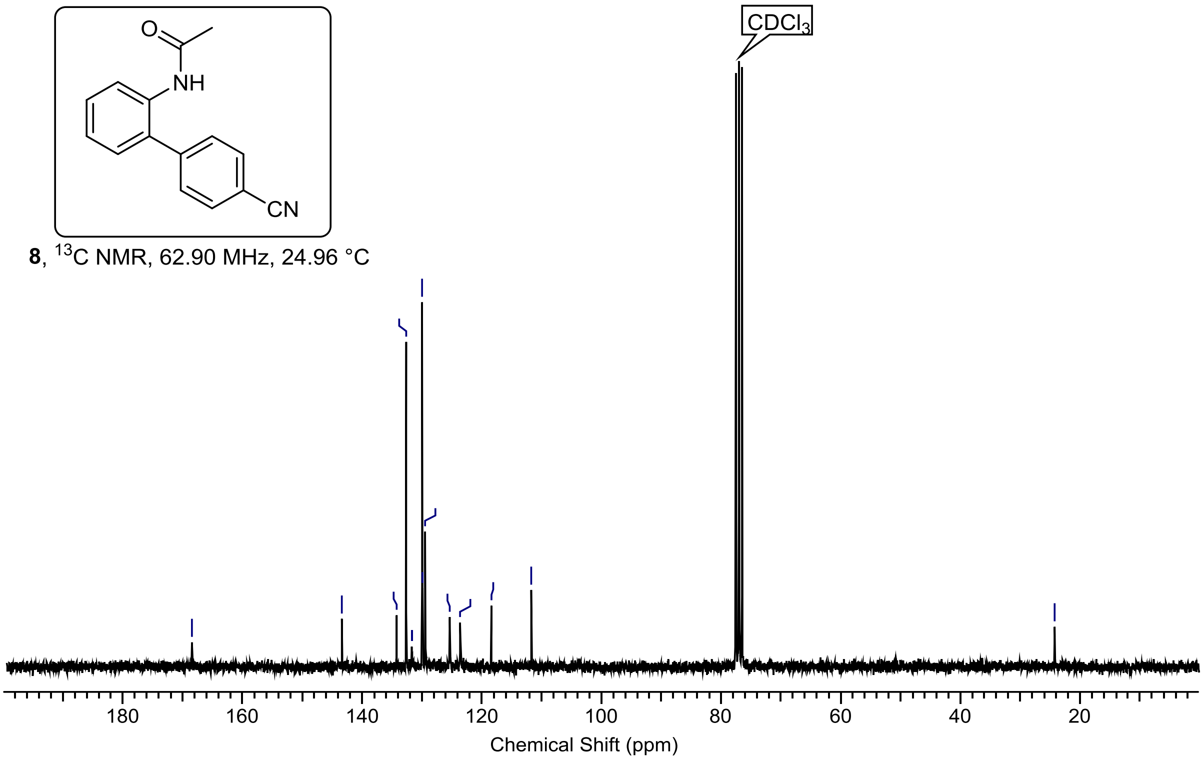
3d, ^{1}H NMR, 300.13 MHz, 25.36°C



3d, ^{13}C NMR, 75.47 MHz, 25.360°C



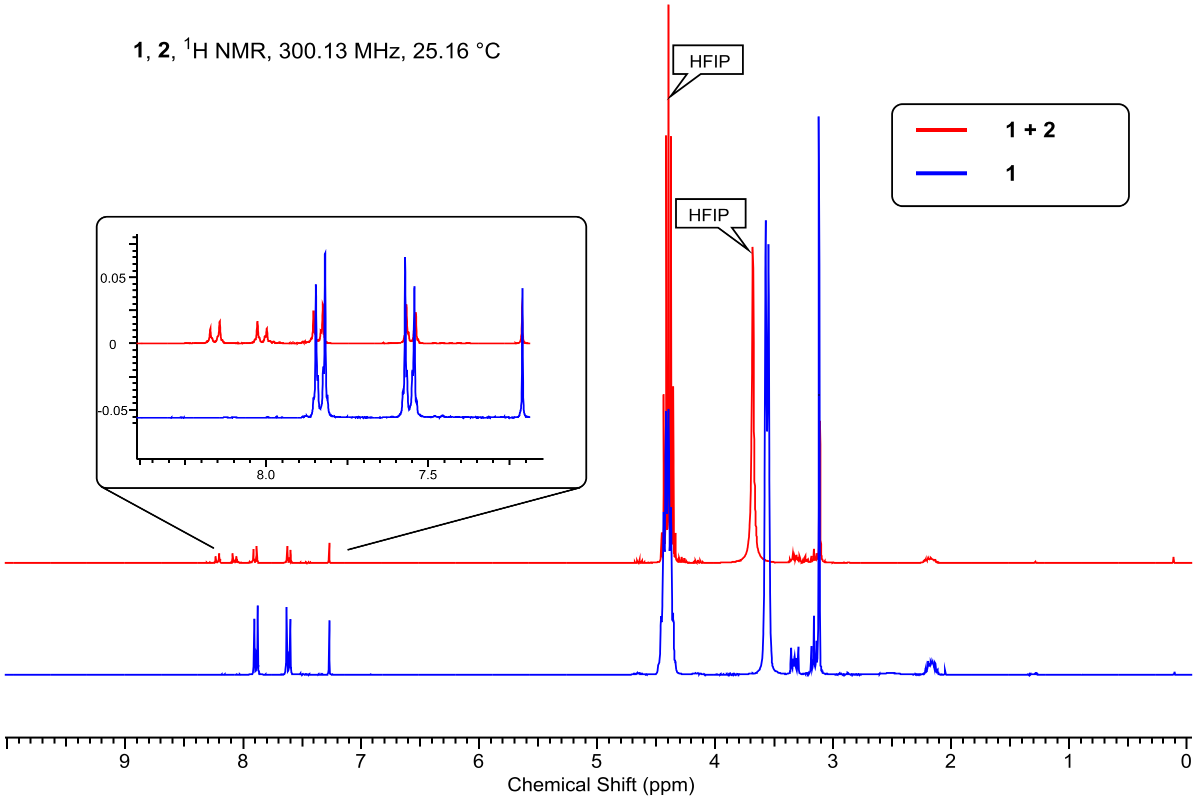
8, ^{1}H NMR, 250,16 MHz, 24.96 °C



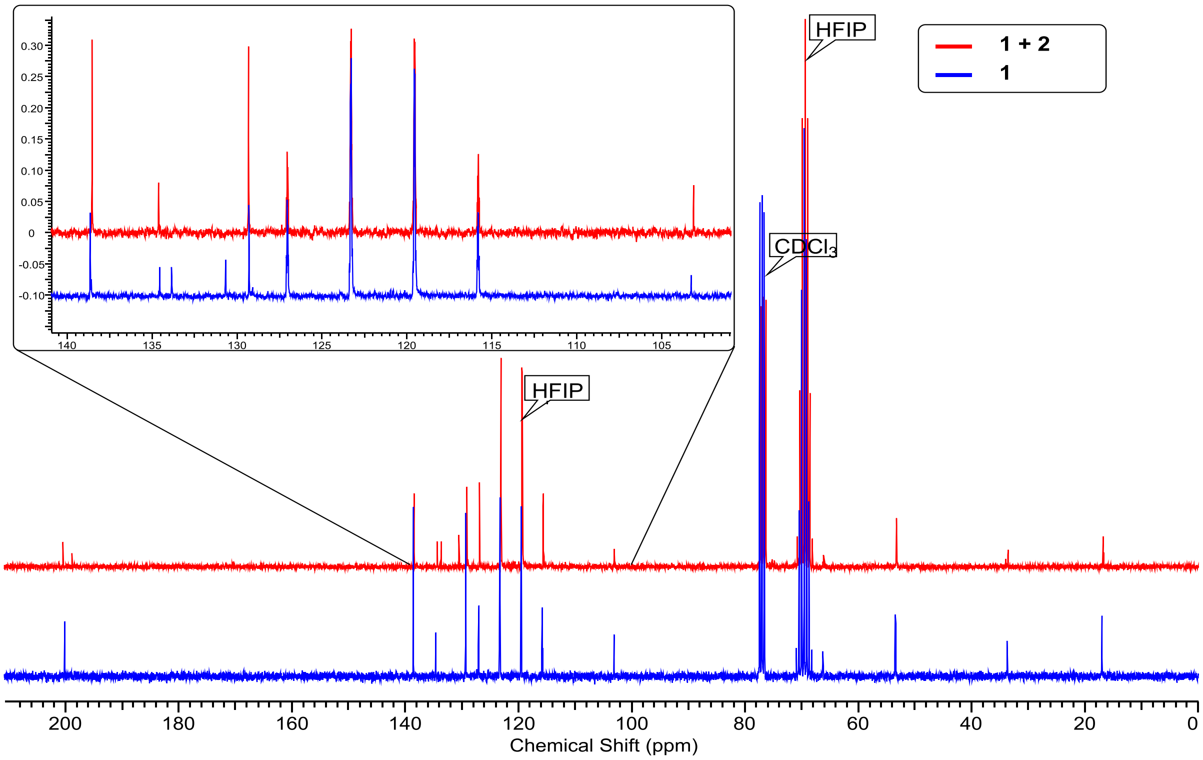
8, ^{13}C NMR, 62.90 MHz, 24.96 °C

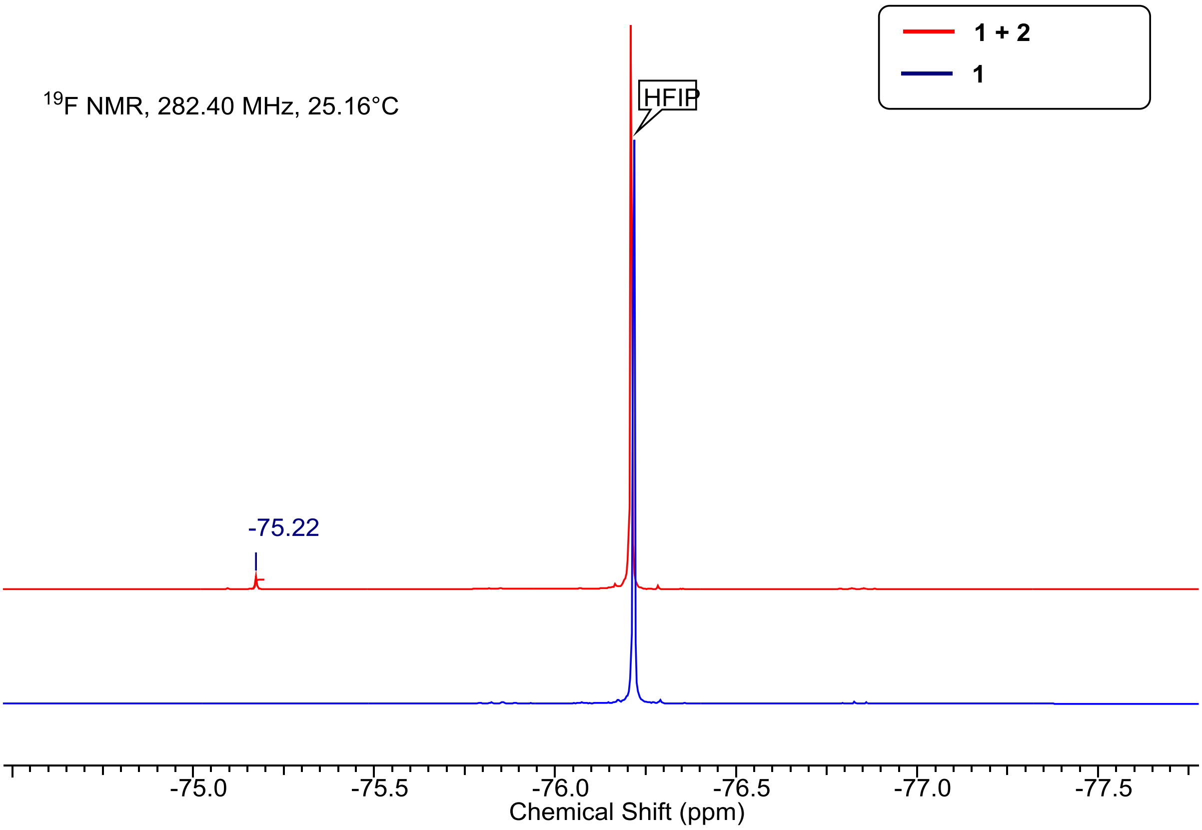
5.3 Electrogeneration of species 2b

1, **2**, ^{1}H NMR, 300.13 MHz, 25.16 °C



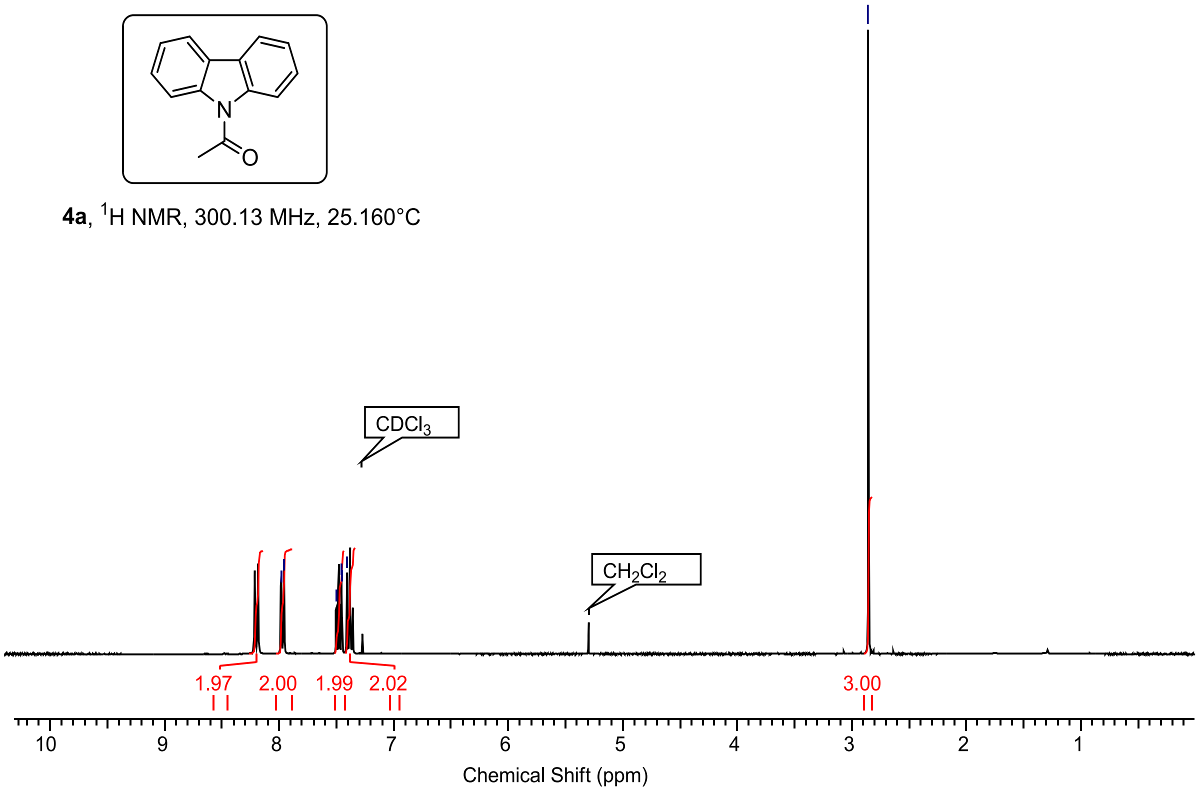
1, **2**, ^{13}C NMR, 74.57 MHz, 25.16 °C



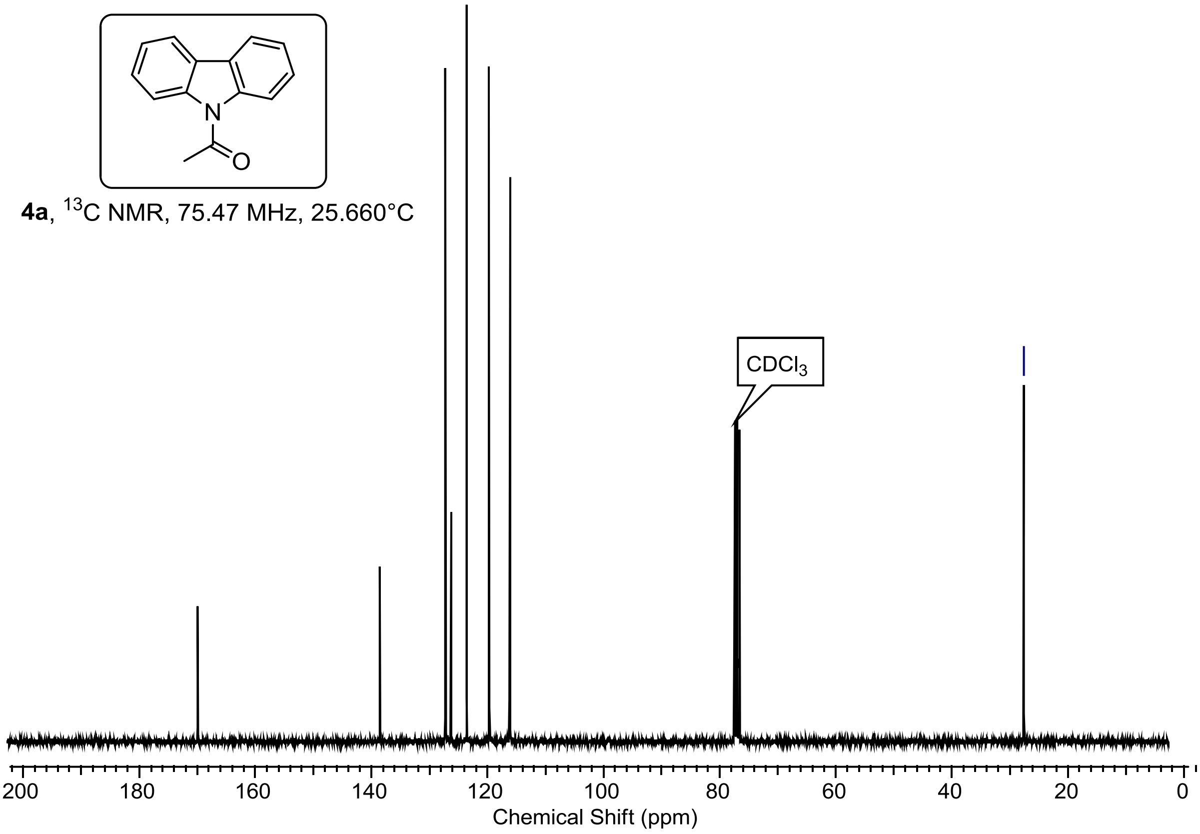


19F NMR, 282.40 MHz, 25.16°C
1 + 2
1
HFIP
-75.22
-75.0
-75.5
-76.0
-76.5
-77.0
-77.5
Chemical Shift (ppm)

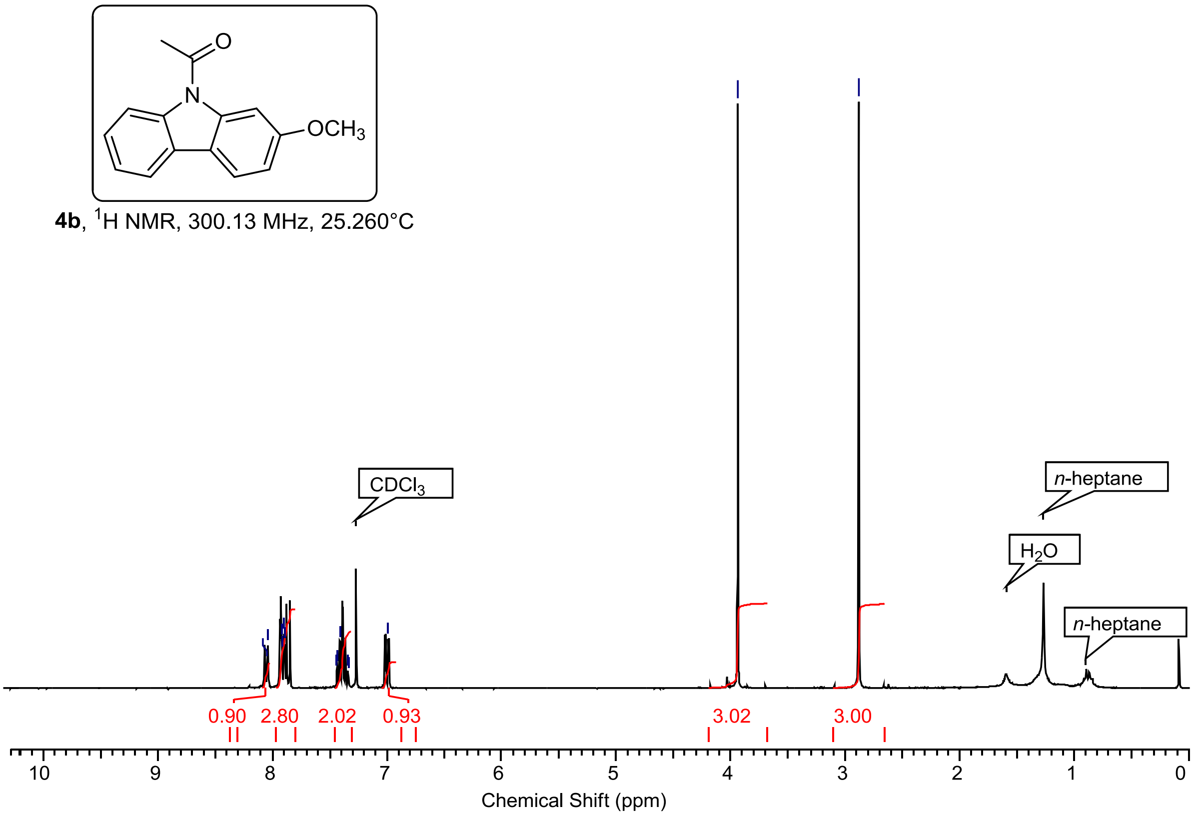
5.4 Oxidative C-N coupling reactions using electrogenerated 2b



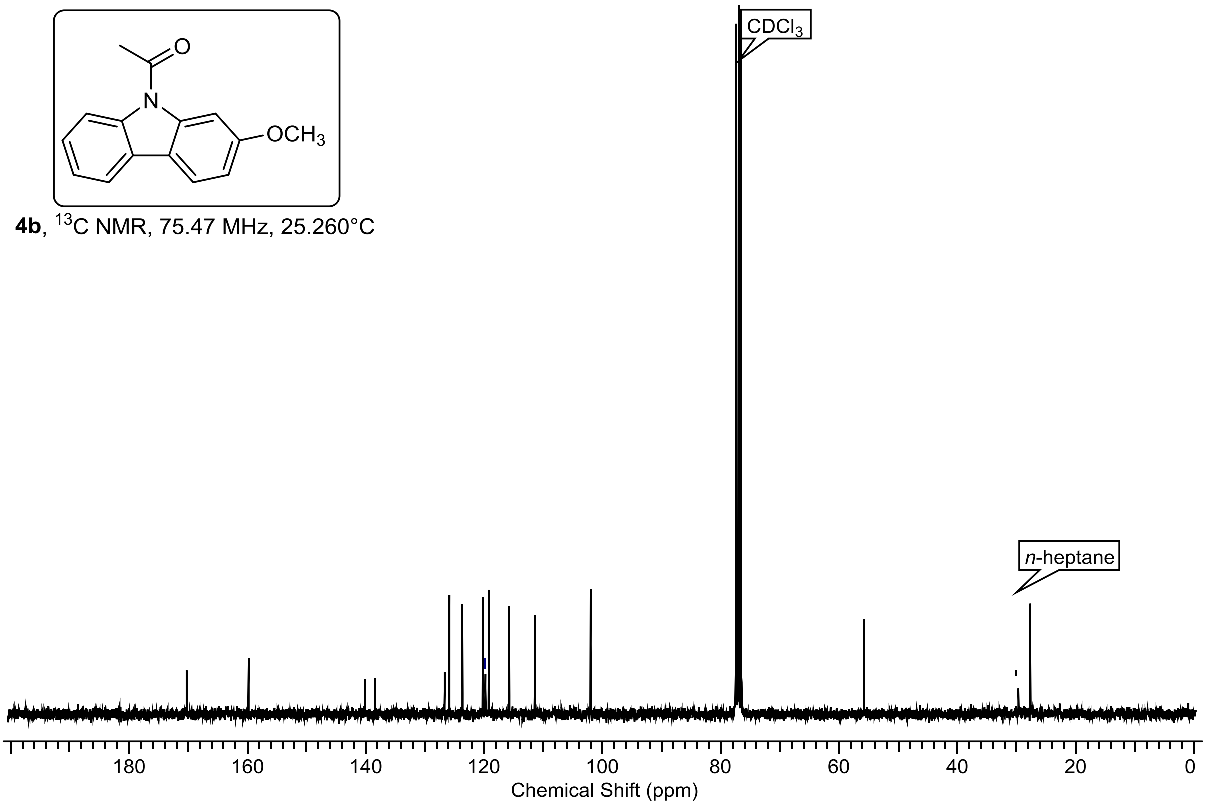
4a, ^{1}H NMR, 300.13 MHz, 25.160°C



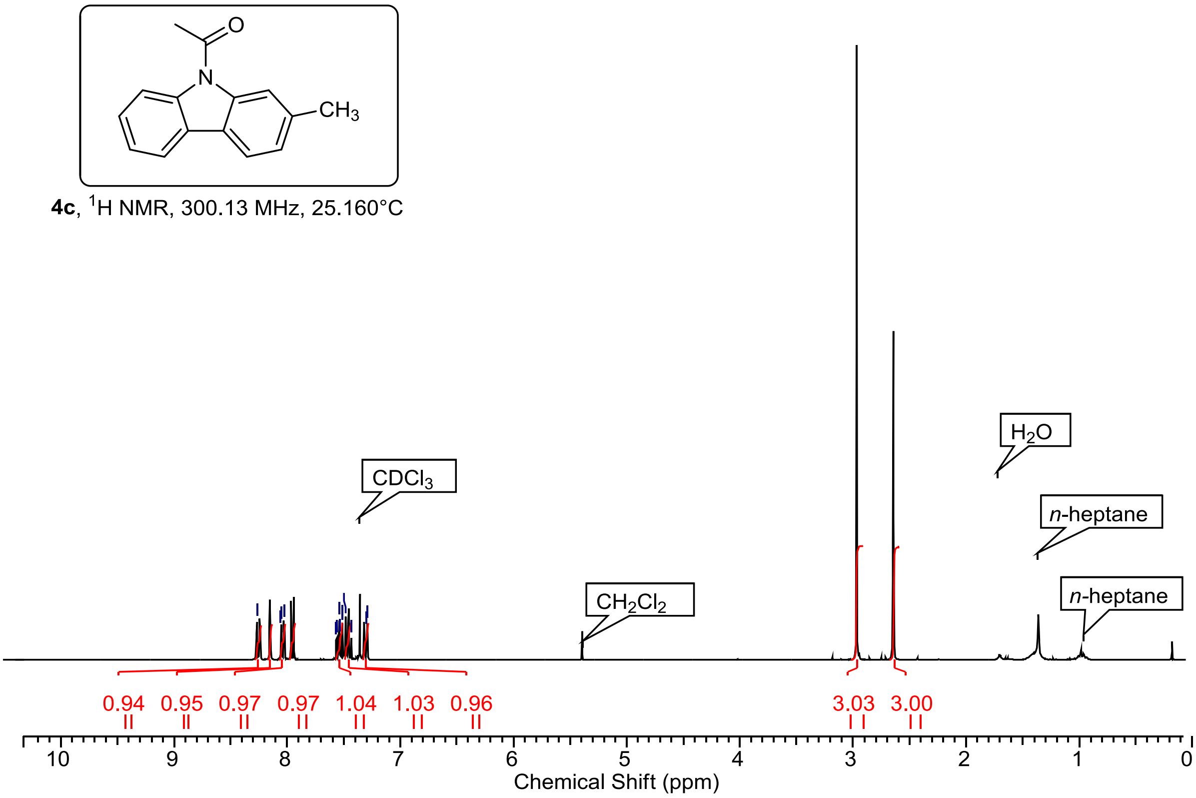
4a, ^{13}C NMR, 75.47 MHz, 25.660°C



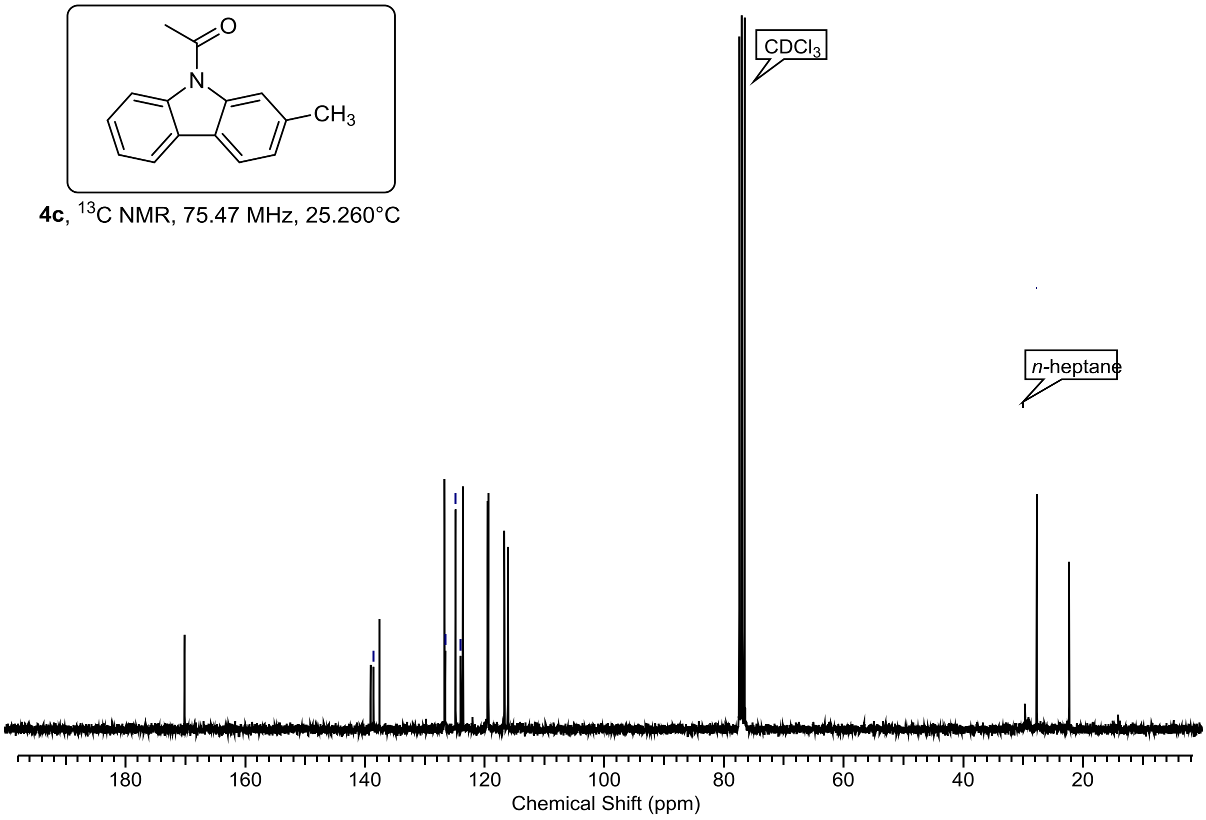
4b, ^{1}H NMR, 300.13 MHz, 25.260°C



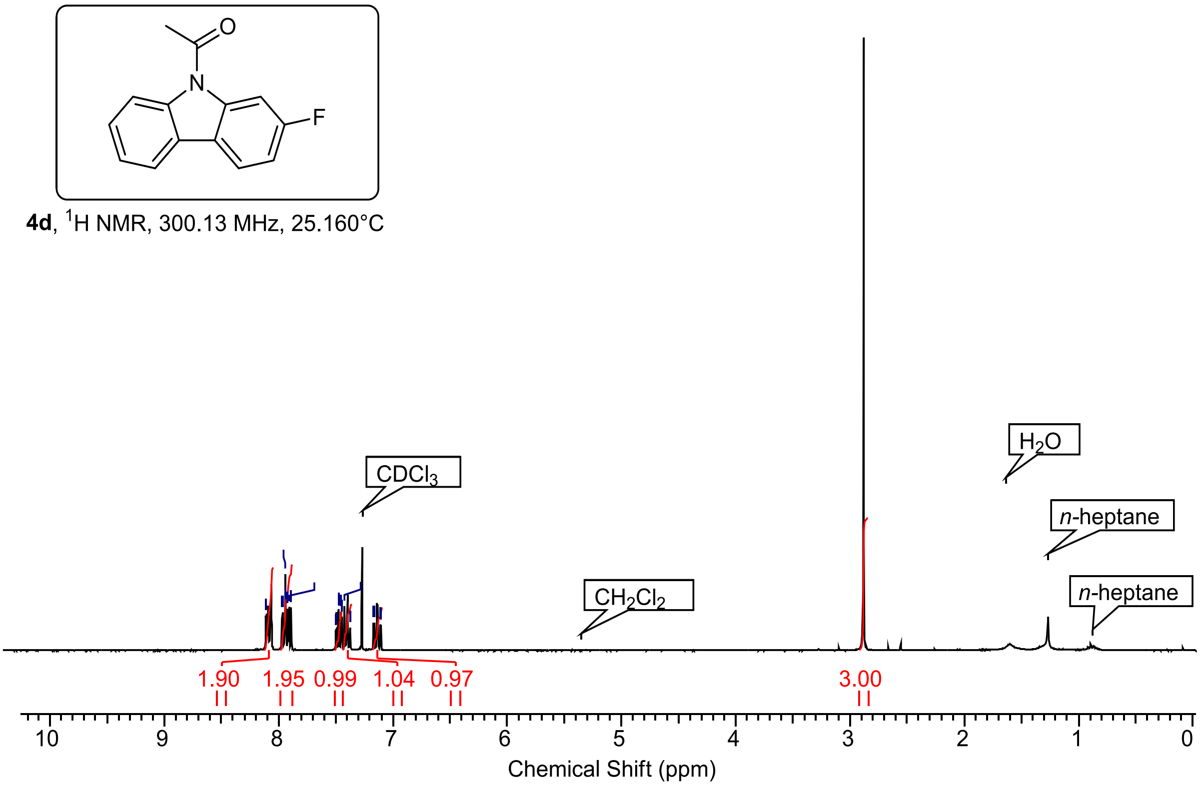
4b, ^{13}C NMR, 75.47 MHz, 25.260°C



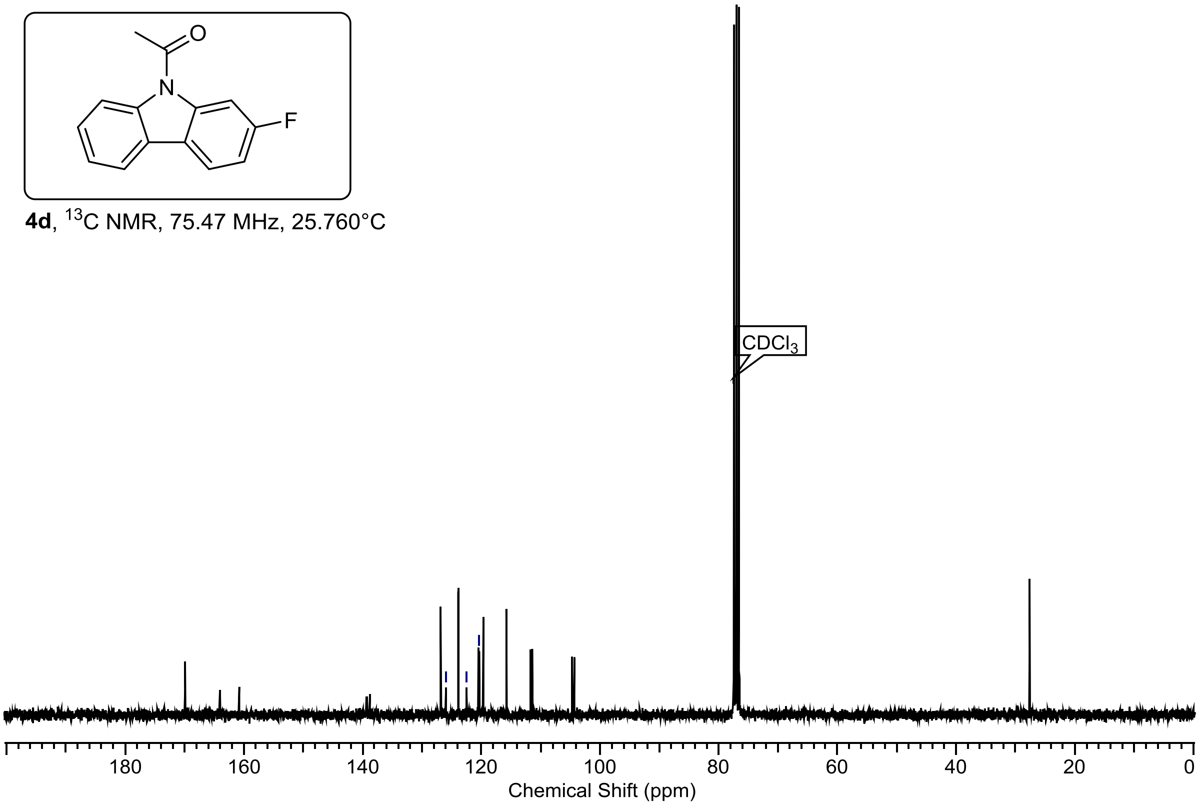
4c, ^{1}H NMR, 300.13 MHz, 25.160°C



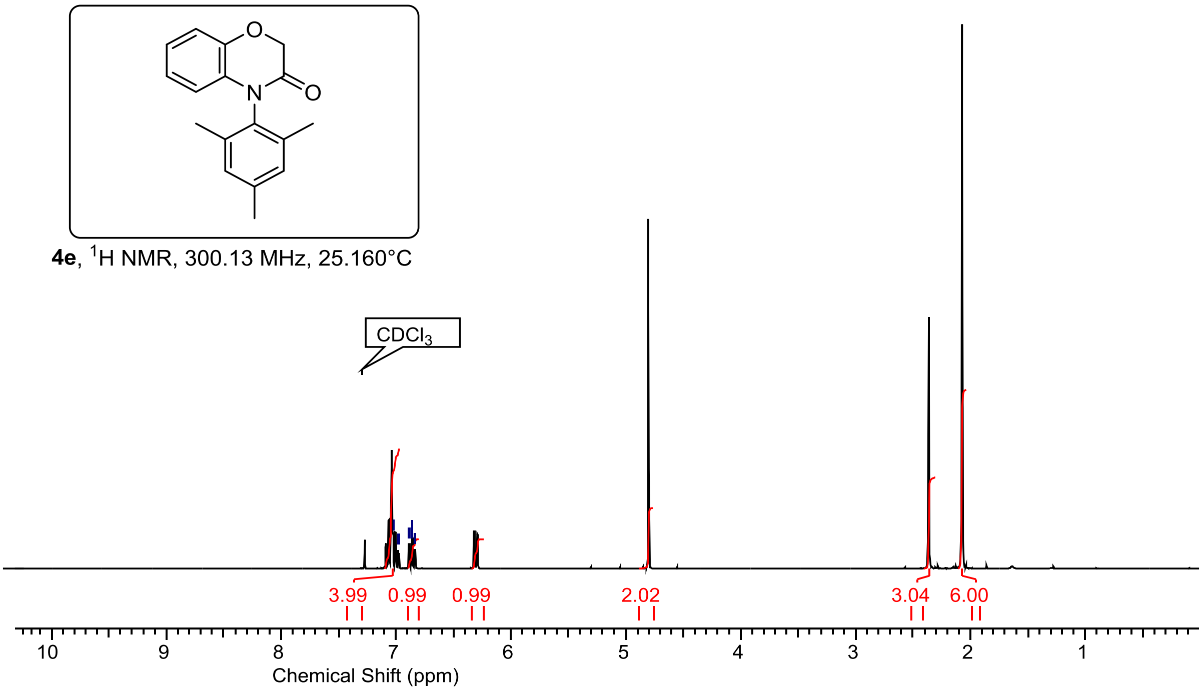
4c, ^{13}C NMR, 75.47 MHz, 25.260°C



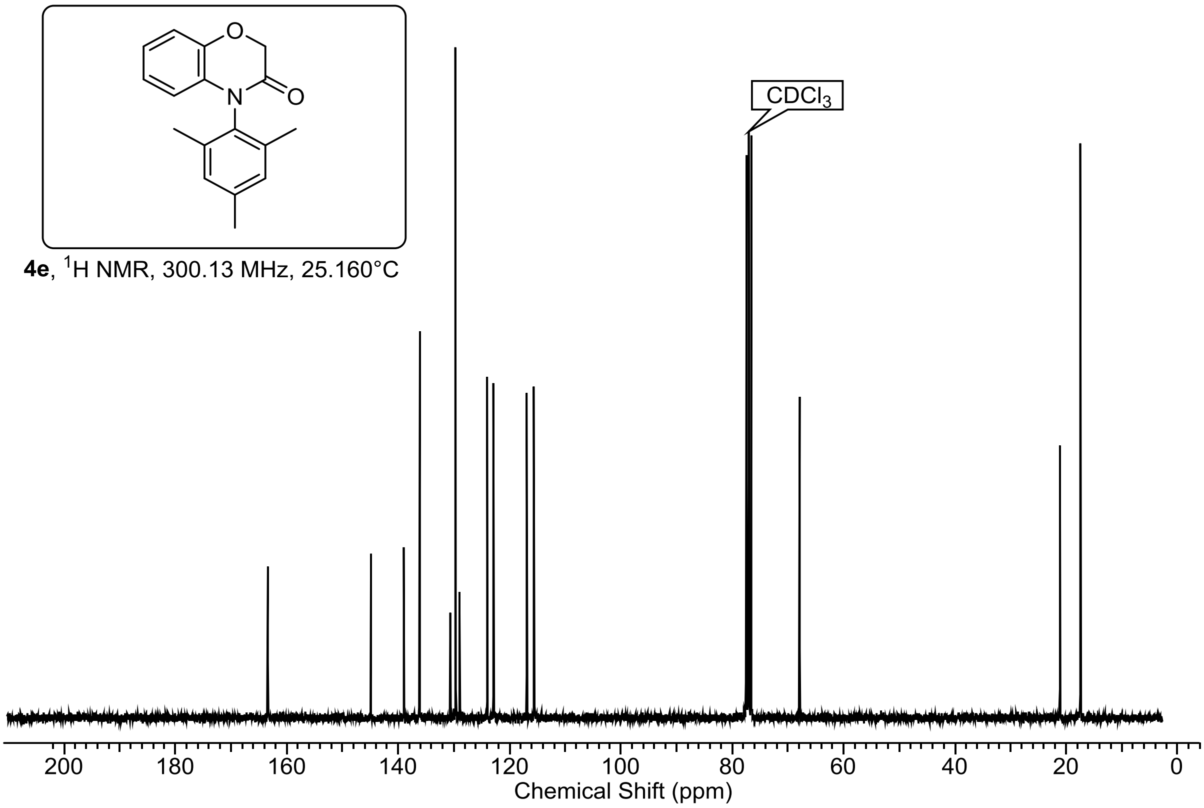
4d, ^{1}H NMR, 300.13 MHz, 25.160°C



4d, ^{13}C NMR, 75.47 MHz, 25.760°C

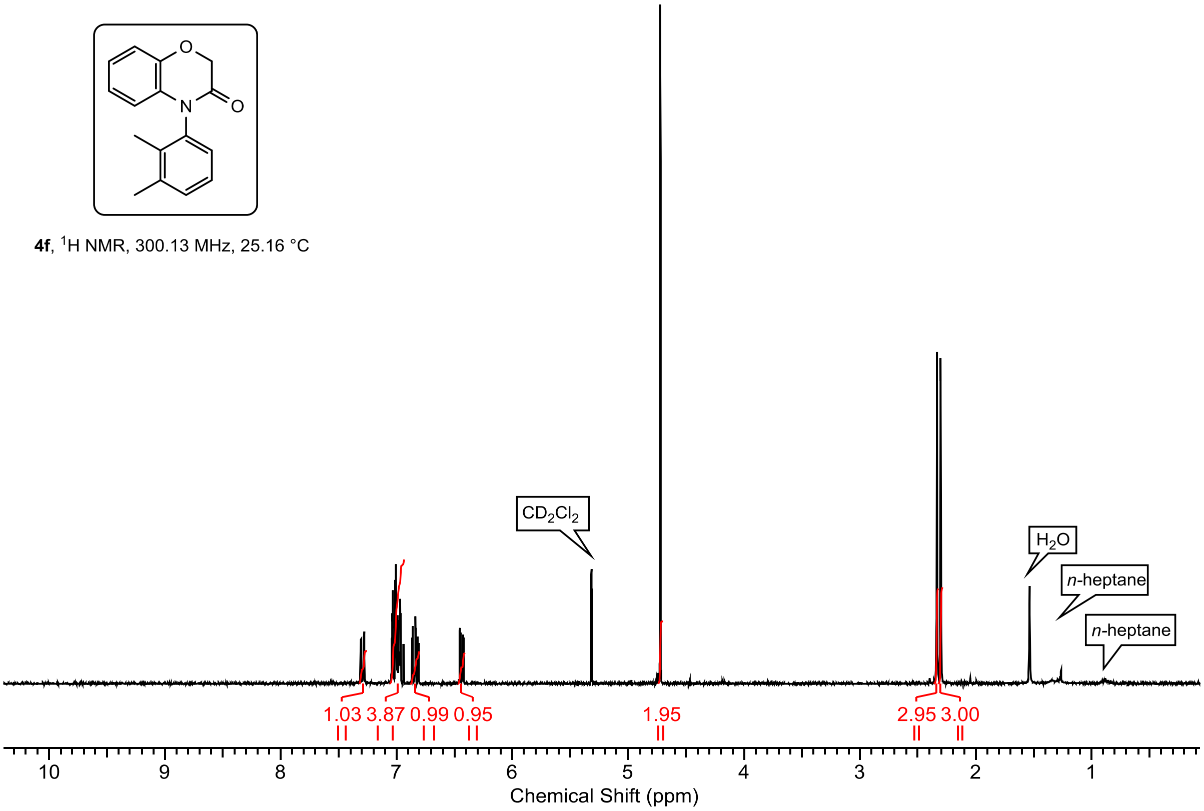


4e, ^{1}H NMR, 300.13 MHz, 25.160°C

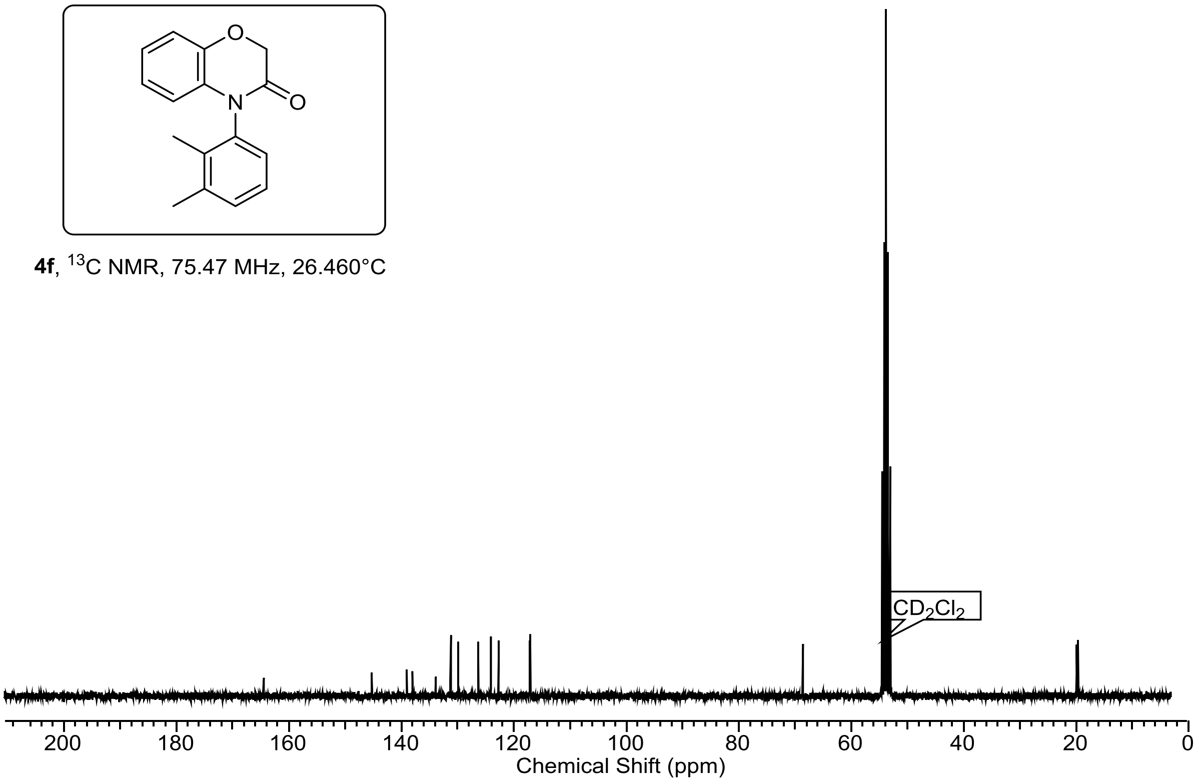


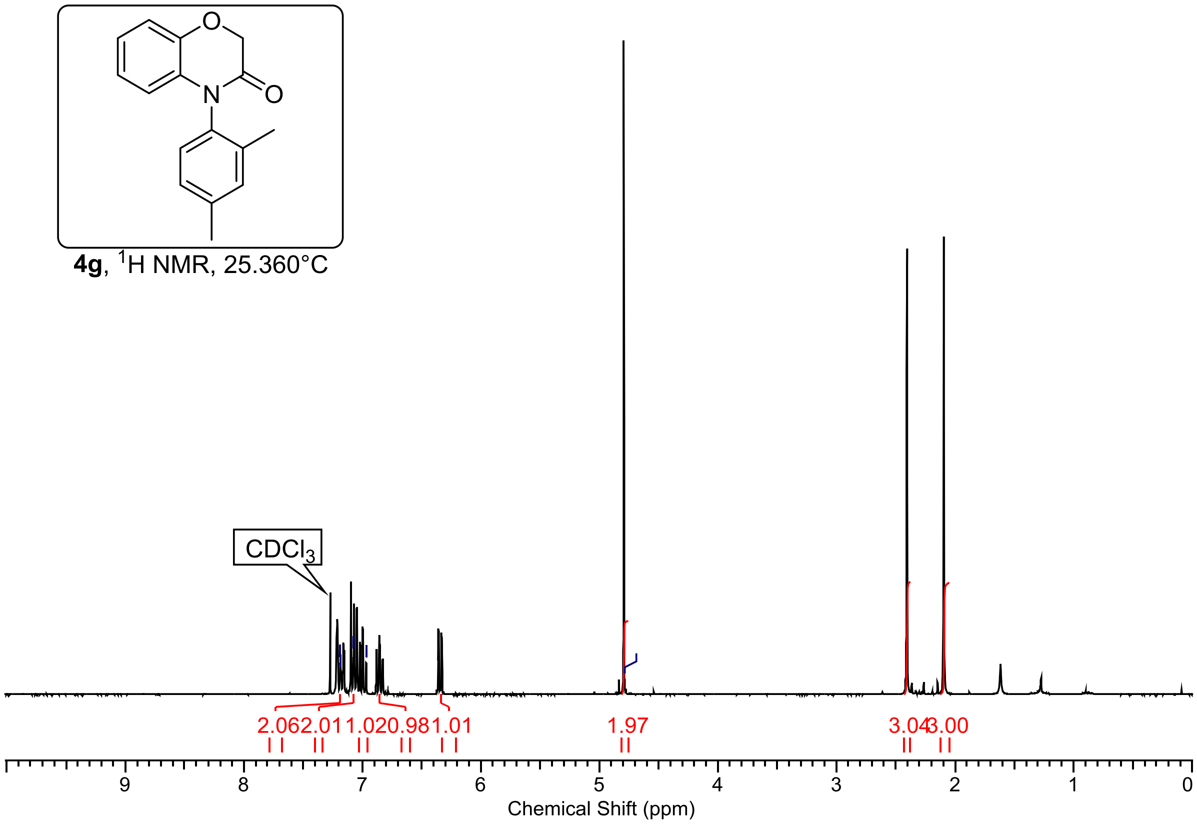
4e, ^{1}H NMR, 300.13 MHz, 25.160°C

4f, ^{1}H NMR, 300.13 MHz, 25.16 °C

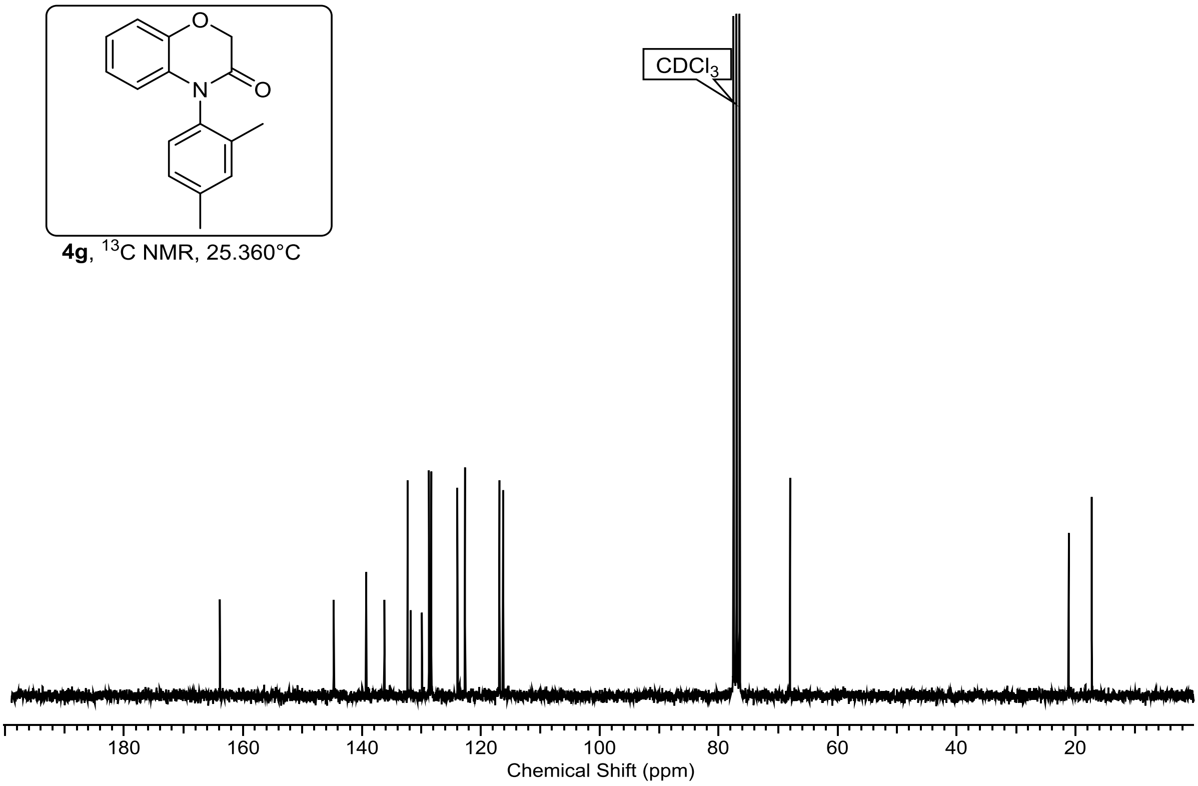


4f, ^{13}C NMR, 75.47 MHz, 26.460°C

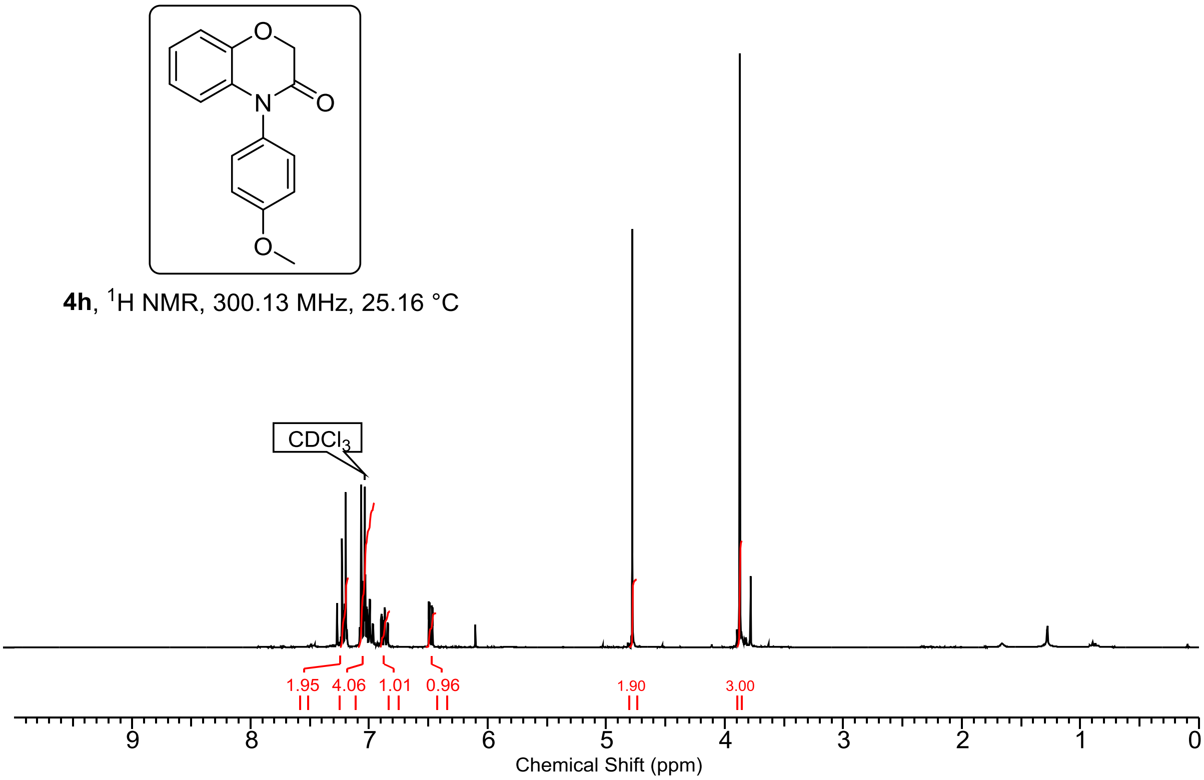




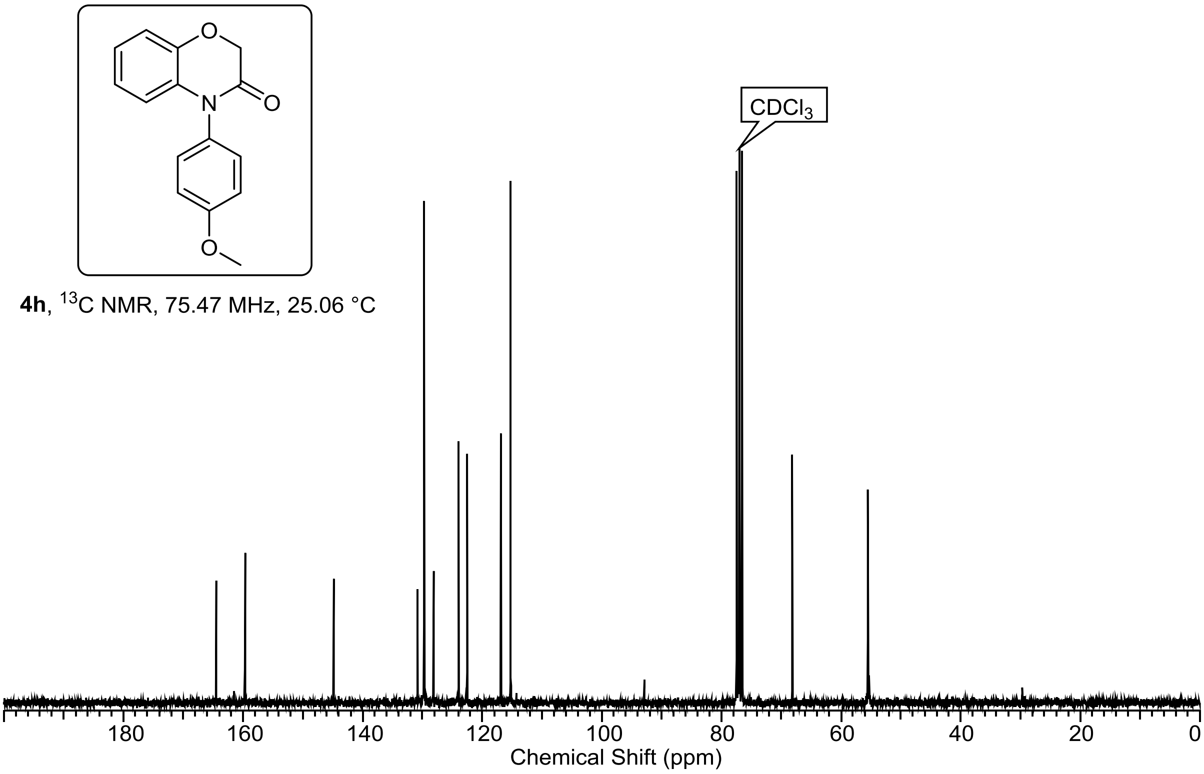
4g, ^{1}H NMR, 25.360°C



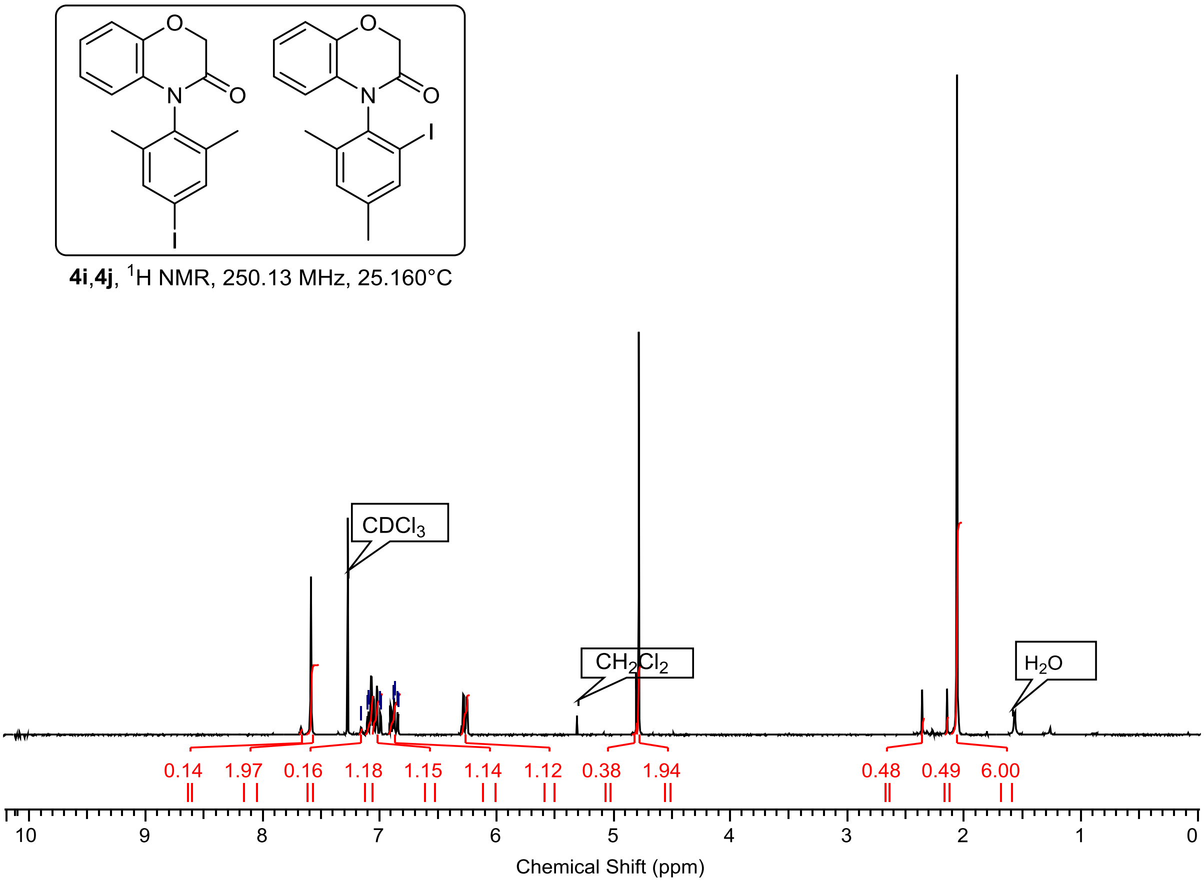
4g, ^{13}C NMR, 25.360°C



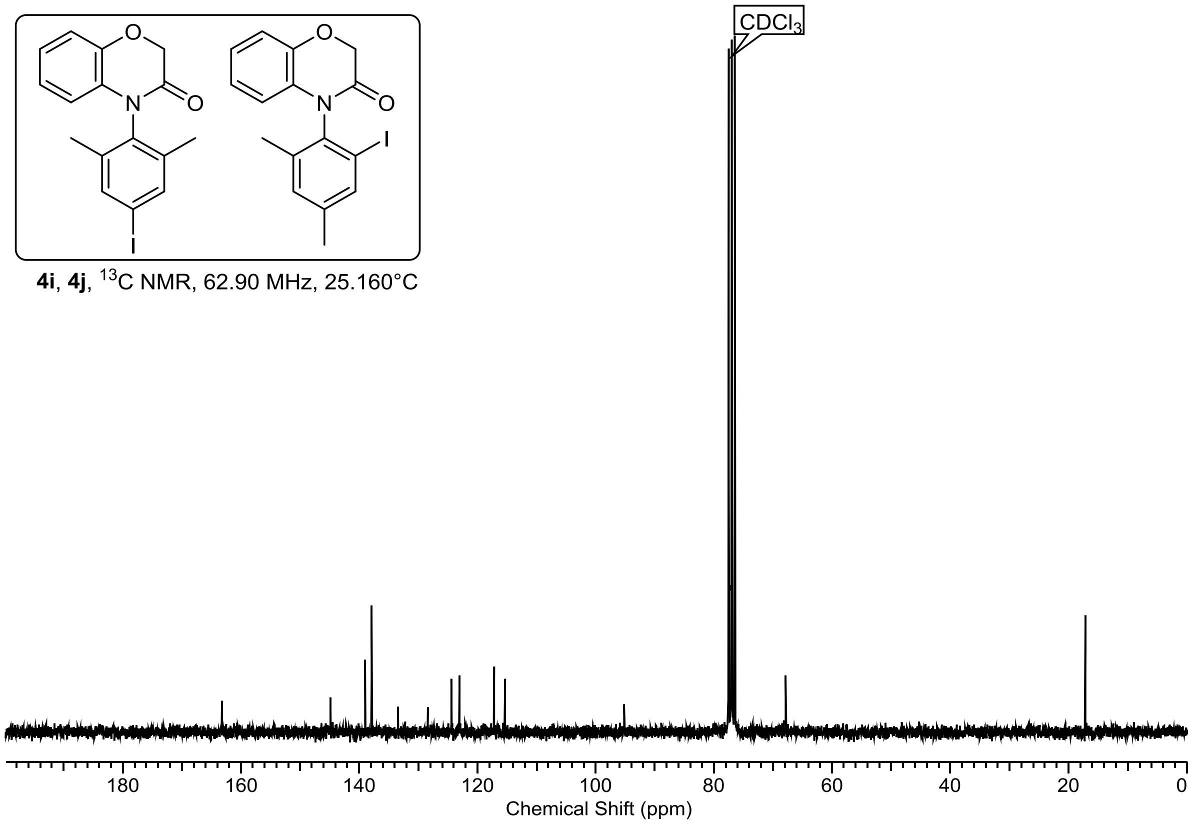
4h, ^{1}H NMR, 300.13 MHz, 25.16 °C



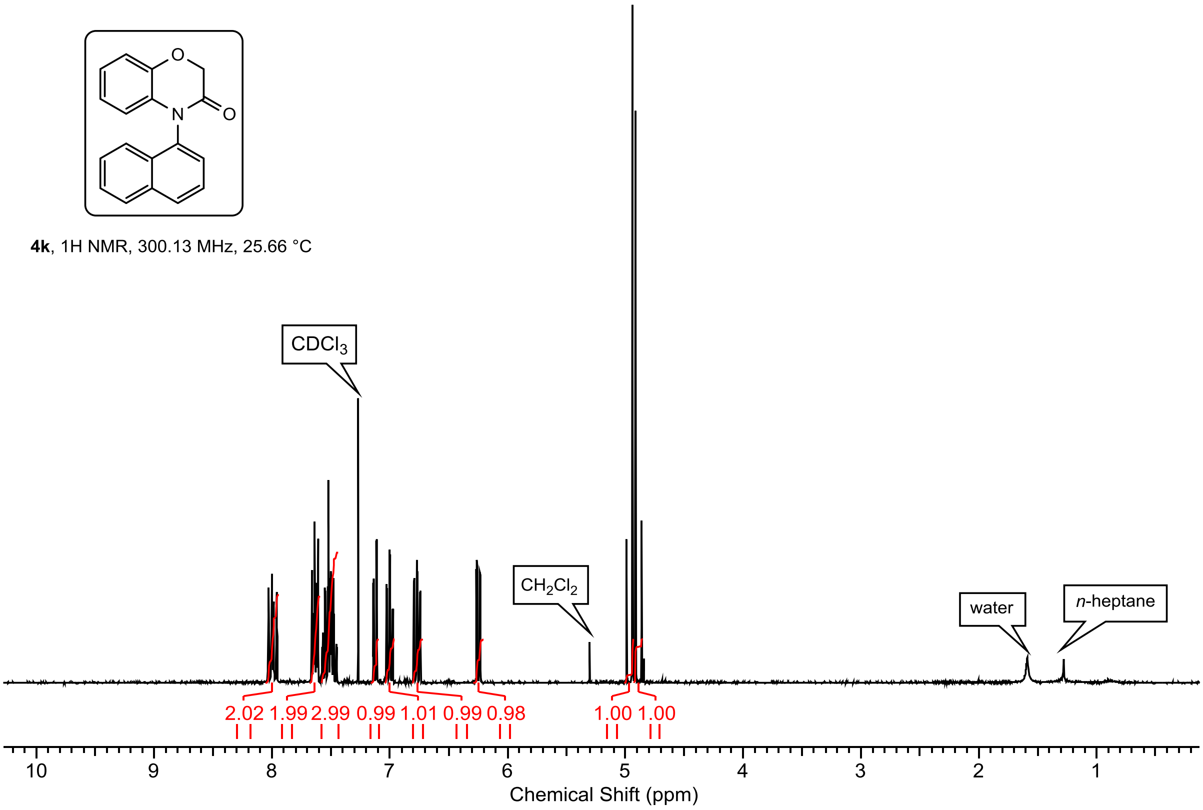
4h, ^{13}C NMR, 75.47 MHz, 25.06 °C

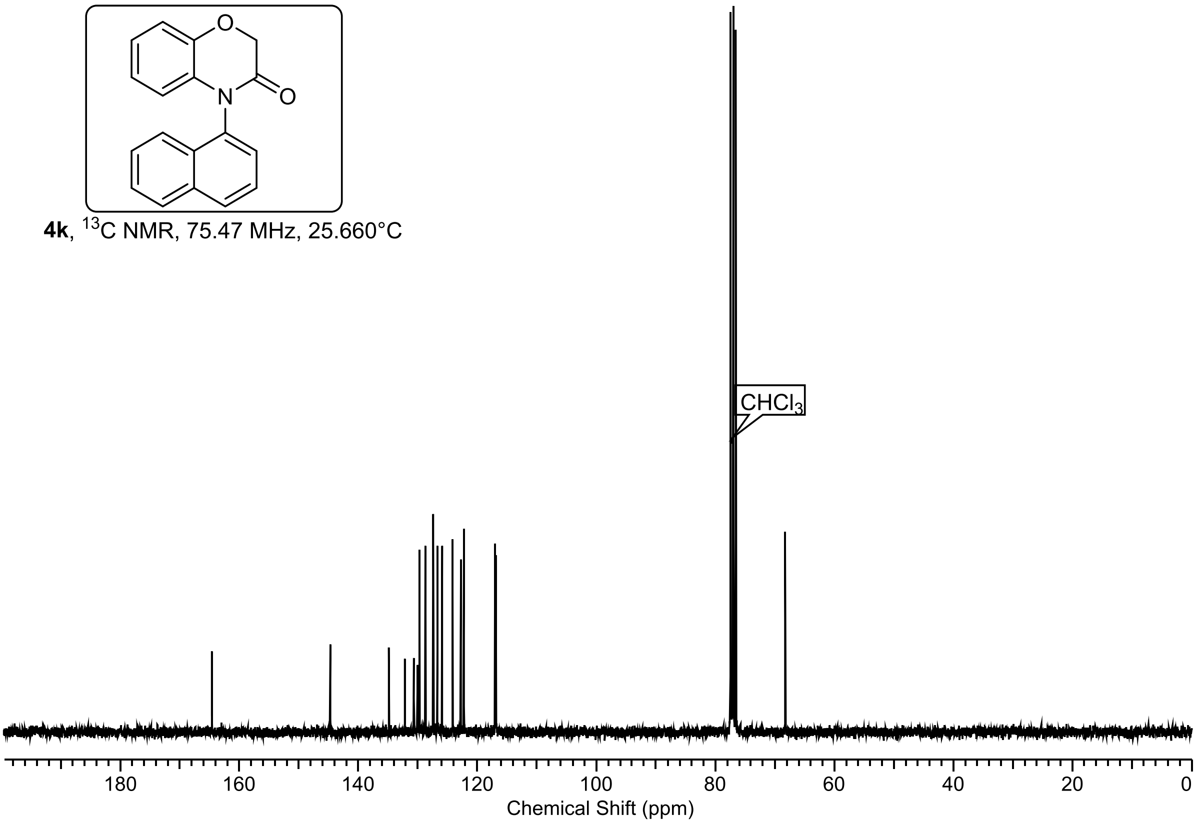


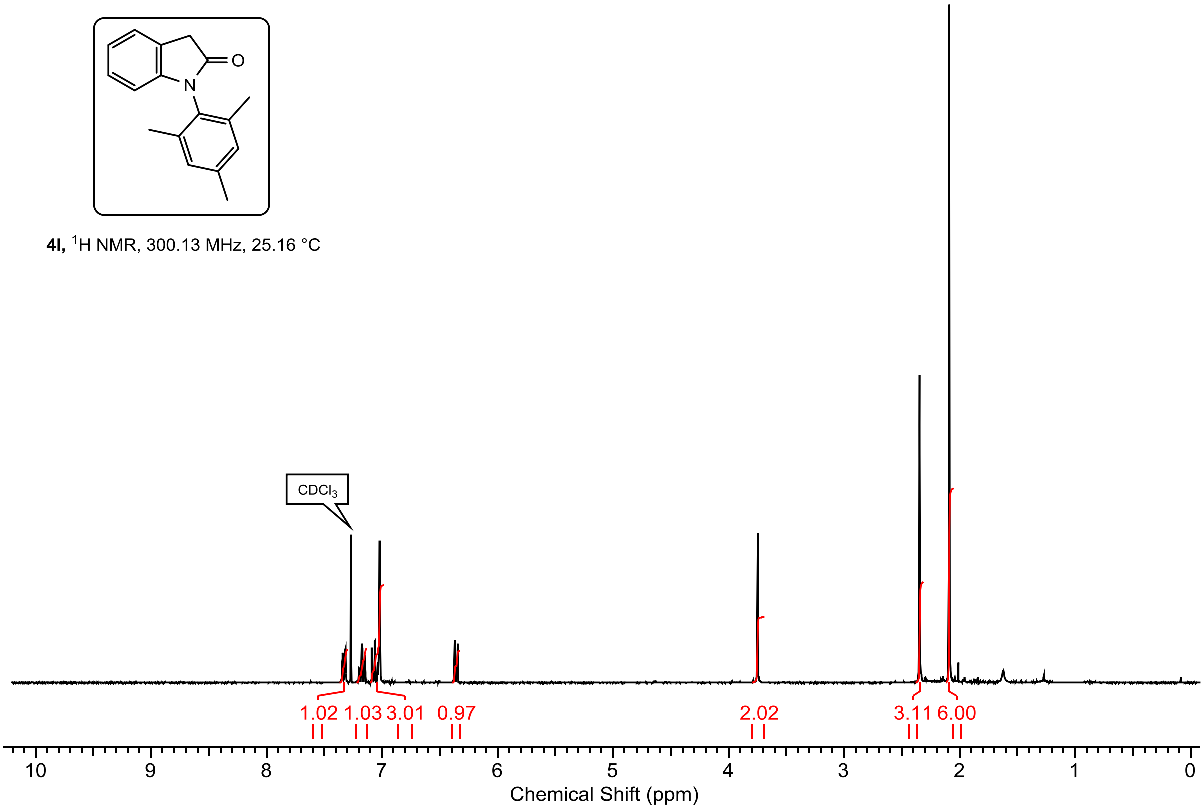
4i,**4j**, ^{1}H NMR, 250.13 MHz, 25.160°C



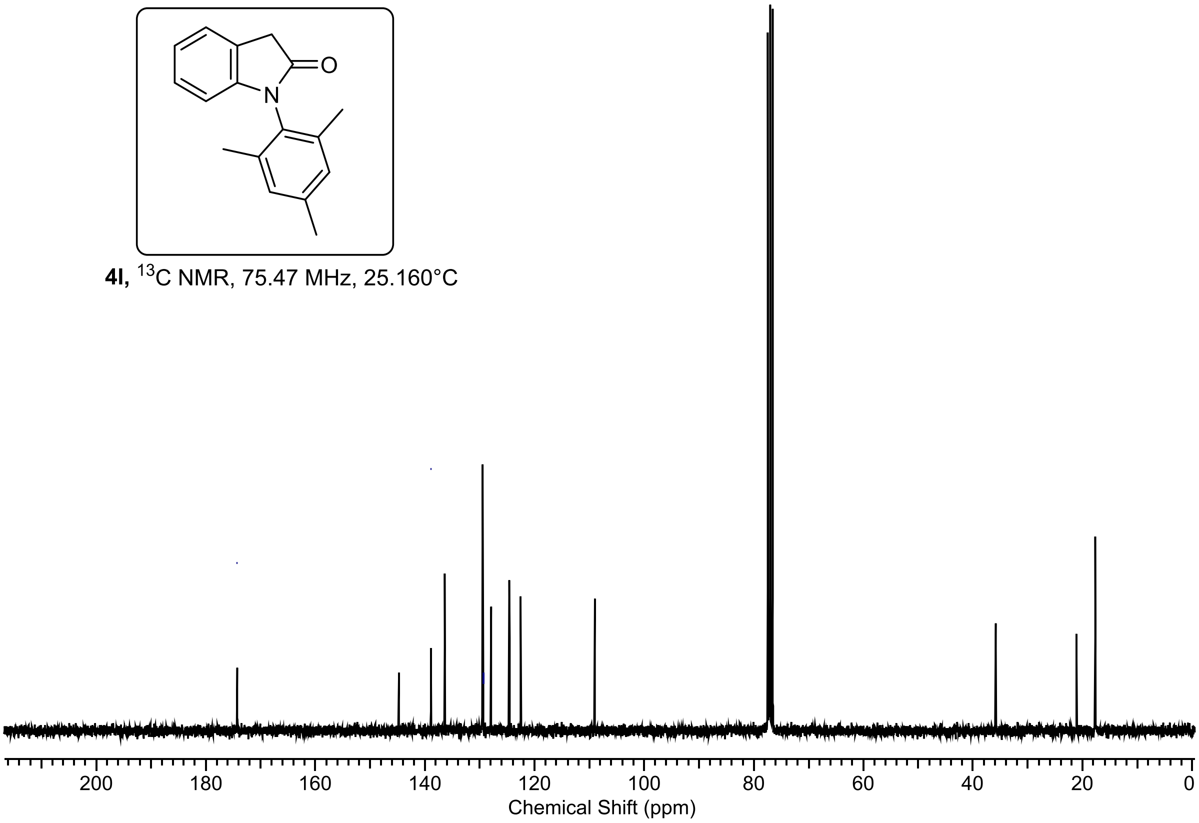
4i, **4j**, ^{13}C NMR, 62.90 MHz, 25.160°C


4k, 1H NMR, 300.13 MHz, 25.66 °C

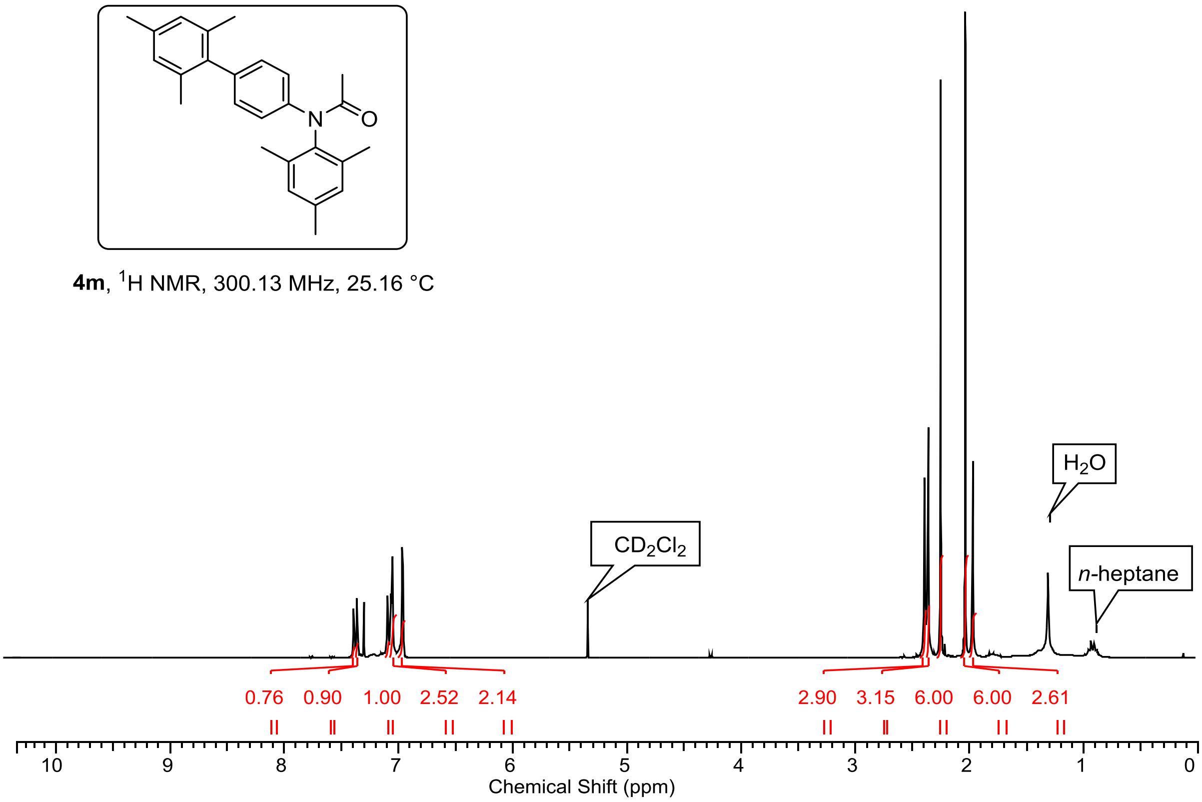

4k, ^{13}C NMR, 75.47 MHz, 25.660°C



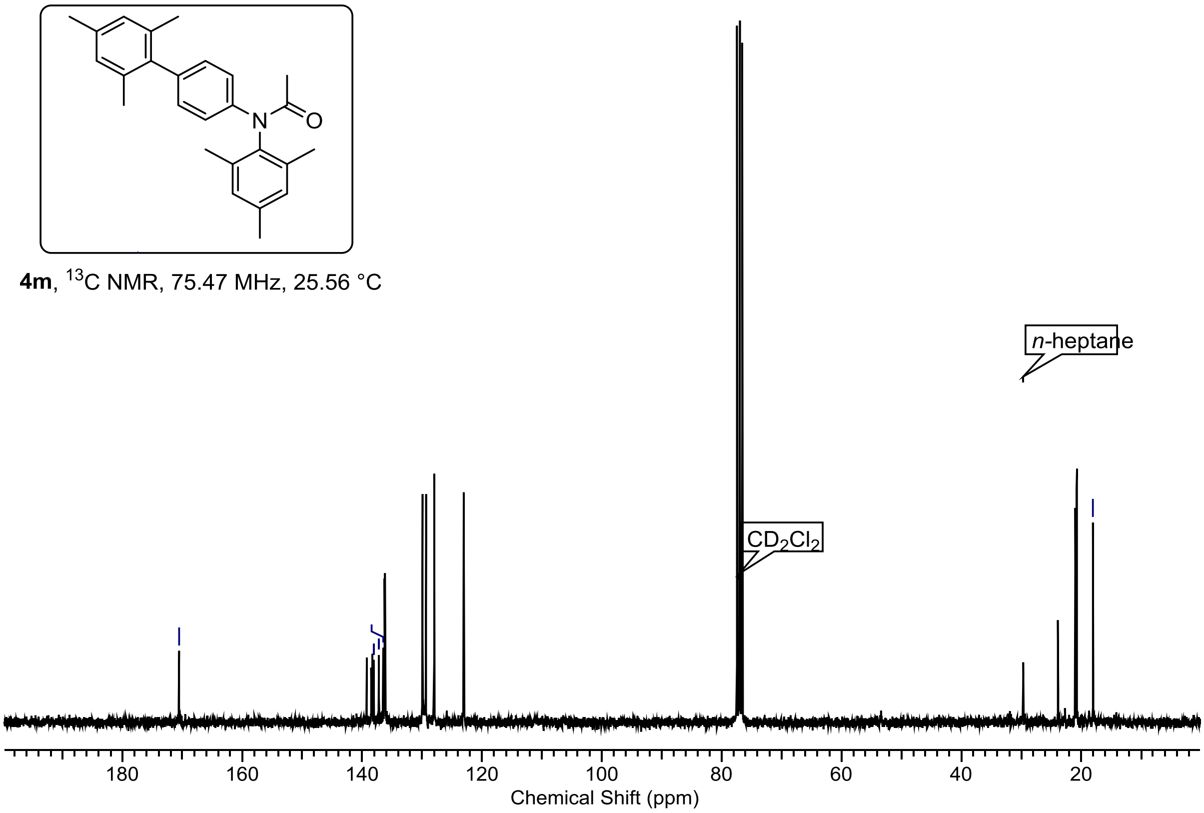
4l, ^{1}H NMR, 300.13 MHz, 25.16 °C



4l, ^{13}C NMR, 75.47 MHz, 25.160°C



4m, ^{1}H NMR, 300.13 MHz, 25.16 °C



4m, ^{13}C NMR, 75.47 MHz, 25.56 °C

6. Optimization of the electrolysis parameters

Table S1: Optimization of current density.

entry	*j* [mAcm^{-2}]	*FE** [%]
1	7.5	34
2	15	71
3	30	32

Conditions: Undivided batch cell, WE= glassy carbon plate (immersed surface: A = 1.0 cm^2), CE = platinum sheet, argon atmosphere, exclusion of light, room temperature, V(electrolyte) = 5 mL, c(**1**) = 0.2 M, solvent = HFIP, Q = 1 F mol^{-1} mediator **1**. *determined by integration of the aromatic signals of **1** and **2b** in the ^{1}H NMR spectra.

Table S2: Upscaling of the electrolysis.

entry	*V* [mL]	*FE** [%]
1	5	71
2	10	67
3	50	38

Conditions: Undivided batch cell, WE= glassy carbon plate (immersed surface: A = 1.0 cm^2), CE = platinum sheet, argon atmosphere, exclusion of light, room temperature, j = 15 mA cm^{-2}, c(**1**) = 0.2 M, solvent = HFIP, Q = 1 F mol^{-1} mediator **1**. *determined by integration of the aromatic signals of **1** and **2b** in the ^{1}H NMR spectra.

Table S3: Influence of the mediator salt concentration.

entry	*c*(1) [M]	*FE** [%]
1	0.1	37
2	0.2	67
3	0.5	58

Conditions: Undivided batch cell, WE = glassy carbon plate (immersed surface: A = 1.0 cm^2), CE = platinum sheet, argon atmosphere, exclusion of light, room temperature, j = 15 mA cm^{-2}, V(electrolyte) = 10 mL, Q = 1 F mol^{-1} mediator **1**. *determined by integration of the aromatic signals of **1** and **2b** in the ^{1}H NMR spectra.

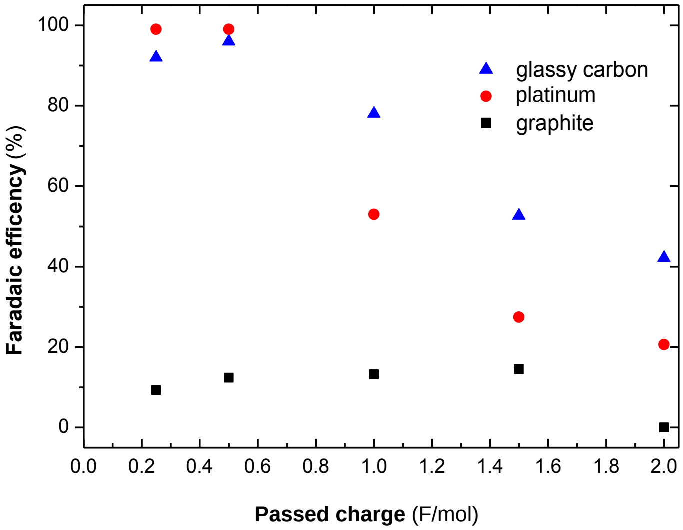


Figure S1: Influence of the working electrode material on the Faradaic efficiency of the generation of **2b**. Conditions: Undivided batch cell, WE= glassy carbon plate (immersed surface *A* = 1.0 cm^2), CE = platinum sheet, argon atmosphere, exclusion of light, room temperature, *j* = 15 mA cm^{-2}, *V*(electrolyte) = 10 mL, *c*(**1**) = 0.2 M. The Faradaic yield was determined by integration of the aromatic signals of **1** and **2b** in the ^{1}H NMR spectra.

7. Conductivity measurements

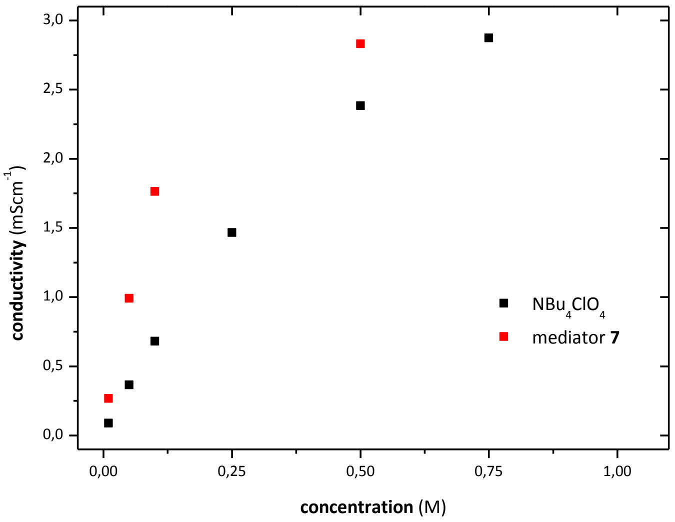


Figure S2: Conductivity measurements of mediator **1** in 3,3,3-trifluoroethanol (red points). For comparison, the data of tetrabutylammonium perchlorate is shown (black points). **1** is not soluble at concentrations above 0.5 M.

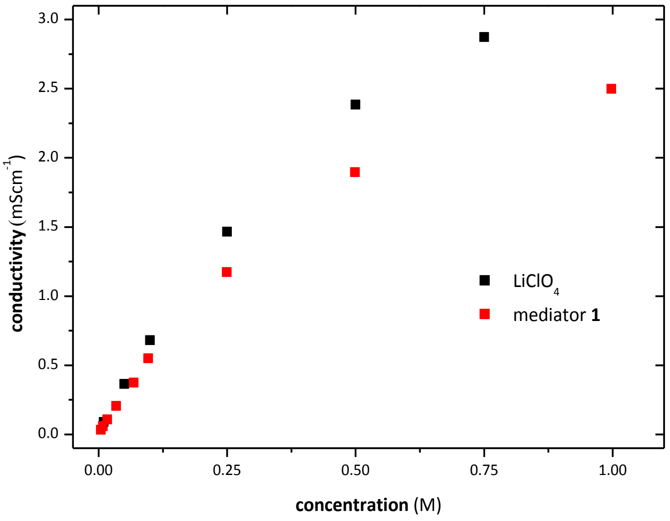


Figure S3: Conductivity measurements of mediator **1** in 1,1,1,3,3,3-hexafluoroisopropanol (red points). For comparison, the data of lithium perchlorate is shown (black points). LiClO4 is not soluble at concentrations above 0.75 M.

8. Attempts for isolation of 2b

Whereas **2b** is stable in HFIP solution for at least several days, we found that isolation of the anodically generated iodine(III) species is not possible due to the limited stability in absence of a donor solvent. Therefore, our attempts for precipitation and crystallization from the electrolyte were unsuccessful. Furthermore, we noticed that the electrochemically generated iodine(III) species loses a major portion of its activity as reagent when it is added as a solid to a solution of a biphenyl substrate **3** in HFIP. In order to investigate the mode of deactivation, a freshly electrolyzed solution of **1** was partitioned for a comparison study. Whereas one fraction was immediately diluted with $CDCl_3$ ($CDCl_3$/HFIP = 5:1, vol/vol) and subjected to ^1H NMR spectroscopy (Figure S4, blue line), HFIP was removed from the other fraction and the residue dried then in vacuum. The remaining solid was again dissolved in HFIP/$CDCl_3$ 5:1 (vol/vol) and a ^1H NMR spectrum was then recorded for comparison (Figure S4, red line). To our surprise, we found no signals related to decomposition products. However, the ratio **2b**/**1** significantly decreases, from 1:1.8 before drying to 1:2.9 after drying, which is in qualitative agreement with the lower reactivity we previously observed during carbazole synthesis. We therefore conclude that deactivation of the iodine(III) species in the solid state occurs either via reduction to **1** or by formation of polymeric networks.

We also note that NMR analysis of the solid residue of the iodine(III) species after removal of HFIP is not possible in common deuterated polar solvents such as CD_3CN and DMSO-d_6 in absence of fluorinated alcohol, since dissolving of the solid in such solvents leads to a violent decomposition reaction.

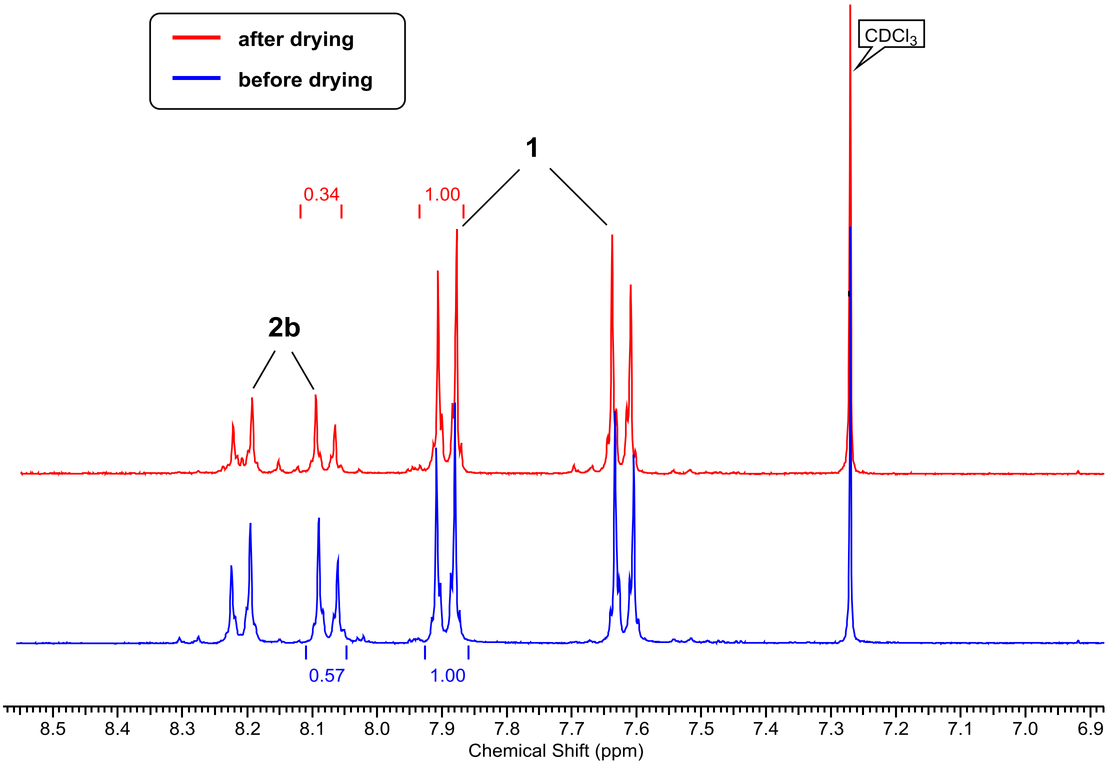


Figure S4. Influence of solvent removal on **2b** studied via ^1H NMR spectroscopy; spectra recorded in $CDCl_3$/HFIP (5:1 vol/vol) at room temperature (300 MHz). Electrolysis was performed as described in general procedure II.

9. References

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(11) Samanta, R.; Lategahn, J.; Antonchick, A. P. *Chem. Commun.* **2012**, *48*, 3194–3196.