−Electronic Supplementary Information−

Nucleophilicity parameters for designing transition metal-free C-C bond forming reactions of organoboron compounds

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1. General

Materials

Commercially available acetonitrile (VWR, Prolabo, HPLC-gradient grade and Acros, 99.9%, Extra Dry, AcroSeal) was used as received. Commercially available THF (Sigma-Aldrich, p.a.) was distilled over sodium prior to use.

The benzhydrylium tetrafluoroborates Ar_2CH^+ BF_4^- were prepared as described before.[S1] 5-methylfuran-2-ylboronic acid **1a** was synthesised as described in the literature.[S2] 2-Methyl-5-(pinacolboryl)furan **1b** (CAS Registry Number: 338998-93-9) is commercially available (ABCR, purity 98 %) and used as received.

Analytics

^{1}H NMR (400 and 300 MHz), ^{13}C NMR (100.6 and 75.5 MHz), and ^{19}F NMR spectra (376.3 MHz) were recorded on Varian NMR systems in CD_3CN or $CDCl_3$. Chemical shifts in ppm refer to the solvent residual signal in CD_3CN (δ_H 1.94, δ_C 1.4 ppm) or $CDCl_3$ (δ_H 7.24, δ_C 77.2 ppm) as internal standard or to external $CFCl_3$ (δ_F 0.0 ppm), respectively. ^{11}B NMR spectra (128.3 MHz) were obtained by using a JEOL ECX-400 spectrometer and referenced to external $BF_3{\cdot}OEt_2$ (0.0 ppm). The following abbreviations were used to describe the mutiplicities of resonances: br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. NMR signal assignments are based on additional 2D-NMR experiments (COSY, HSQC, and HMBC).

Kinetics

The rates of all investigated reactions were determined photometrically. The temperature of the solutions during all kinetic studies was kept constant (20.0 ± 0.1°C) by using a circulating bath thermostat. The kinetic experiments were carried out with freshly prepared stock solutions of **1** in CH_3CN. The electrophiles **2** and **9**–**13** (also prepared as stock solutions in CH_3CN if not mentioned otherwise) were always employed as minor component in the reactions with the nucleophiles **1**, resulting in first-order kinetics.

The rates of slow reactions ($t_{1/2}$ > 15-20 s) were determined by using a J&M TIDAS diode array spectrophotometer controlled by Labcontrol Spectacle software and connected to a Hellma 661.502-QX quartz Suprasil immersion probe (5 mm light path) via fiber optic cables and standard SMA connectors. For the evaluation of fast kinetics ($t_{1/2}$ < 20 s) the stopped-

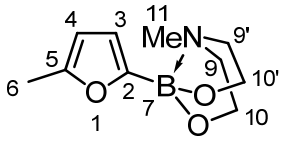
flow spectrophotometer system Applied Photophysics SX.18MV-R stopped-flow reaction analyser was used.

Rate constants k_{obs} (s^{-1}) were obtained by fitting the single exponential $A_t = A_0 \exp(-k_{obs}t) + C$ (exponential decrease if not mentioned otherwise) to the observed time-dependent absorbance (averaged from at least 5 kinetic runs for each nucleophile concentration in case of stopped-flow methodology). Second-order rate constants k_2 (M^{-1} s^{-1}) were derived from the slopes of the linear correlations of k_{obs} with nucleophile concentrations.

2. Preparation of organoboron compounds 1c-g

5-Methyl-2-(*N*-methyl-1,3,6,2-dioxazaborocane)furan (1c)

The 5-methylfuran-2-ylboronic acid **1a** (1.00 mmol, 126 mg) and *N*-methyldiethanolamine (0.999 mmol, 119 mg) were mixed in diethyl ether (5 mL, freshly distilled). The formed precipitate was separated by filtration, washed with diethyl ether (2 × 50 mL), and dried in vacuum (1 × 10^{-3} mbar). The crude product was purified by precipitation from AcOEt/Et_2O mixtures to give **1c** as a yellowish solid (79 mg, 39 %).



Mp. 116-118 °C (AcOEt/Et_2O).

^{1}H NMR (400 MHz, CD_3CN): δ 2.25 (s, 3 H, 6-H), 2.39 (s, 3 H, 11-H), 2.91–2.97 and 3.12–3.18 (m, 4 H, 10-H and 10'-H), 3.87–3.95 (m, 4 H, 9-H and 9'-H), 5.88 (d, J = 2.0 Hz, 1 H, 4-H), 6.29 (d, J = 2.0 Hz, 1 H, 3-H) ppm.

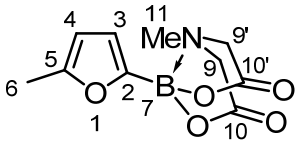
^{13}C NMR (100 MHz, CD_3CN): δ 14.2 (q, C-6), 47.2 (q, C-11), 61.4 (t, C-9, C-9'), 63.0 (t, C-10, C-10'), 106.6 (d, C-4), 117.6 (d, C-3), 154.4 (s, C-5) ppm. C-2 has not been detected.[S3]

^{11}B NMR (128.3 MHz, CD_3CN): δ 10.6 ppm.

(5-Methyl-2-furanyl)boronic acid *N*-methyliminodiacetic ester (1d)

In analogy to the procedure described in reference S3, a two-necked flask was charged with freshly distilled THF (40 mL) and distilled 2-methylfuran (910 mg, 11.1 mmol) under argon. The solution was cooled at –40 °C and *n*-butyllithium (2.1 M in hexane, 4.8 mL, 10 mmol) was added dropwise. The mixture was then allowed to warm progressively to 0 °C within 2 h. After cooling at –78 °C, neat triisopropylborate (2.16 g, 11.5 mmol) was added dropwise

under vigorous stirring and the solution was allowed to warm to 20 °C within 4 h. Subsequently, the mixture was slowly transferred via a cannula into a flask containing *N*-methyliminodiacetic acid (2.1 g, 15 mmol) in DMSO (20 mL) at a temperature of 100 °C. After 2 h the solution was cooled to 20 °C and filtrated through Celite. The solvents were evaporated under vacuum. The residue was crystallised from acetonitrile/diethyl ether solutions to furnish **1d** as an off-white crystalline solid (1.1 g, 42%).



Mp. 135-137 °C (CH_3CN/Et_2O).

^{1}H NMR (400 MHz, CD_3CN): δ 2.29 (s, 3 H, 6-H), 2.63 (s, 3 H, 11-H), 3.88 (d, *J* = 17.0 Hz, 2 H, 9'-H), 4.04 (d, *J* = 17.0 Hz, 2 H, 9-H), 6.02 (d, *J* = 3.1 Hz, 1 H, 4-H), 6.58 (d, *J* = 3.1 Hz, 1 H, 3-H) ppm.

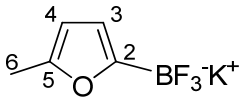
^{13}C NMR (100 MHz, CD_3CN): δ 14.1 (q, C-6), 48.3 (q, C-11), 62.8 (t, C-9 and C-9'), 107.4 (d, C-4), 120.5 (d, C-3), 120.6 (s, C-5), 169.6 (s, C-10 and C-10') ppm. C-2 has not been detected.[S3]

^{11}B NMR (128.3 MHz, CD_3CN): δ 9.7 ppm.

Potassium (5-methylfuran-2-yl)trifluoroborate (1e)

(CAS Registry Number: 1111213-54-7)

Following a procedure described in reference S4, the boronic acid **1a** (756 mg, 6.00 mmol) was dissolved in methanol (5 mL), and the solution was cooled at 0 °C. A concentrated aqueous solution of KHF_2 (1.40 g in 5 mL of water, 18.5 mmol) was added dropwise at 0 °C, and the reaction was allowed to warm at r.t. within 1 h. Then the solvent was removed under vacuum. The crude product was purified by two subsequent crystallisations from acetone/diethyl ether solutions to give **1e** as a colorless solid (680 mg, 62 %).



Mp. 265–267 °C (acetone/Et_2O).

^{1}H NMR (400 MHz, CD_3CN): δ 2.23 (s, 3 H, 6-H), 5.78 (m, 1 H, 4-H), 6.04 (m, 1 H, 3-H) ppm.

^{13}C NMR (100 MHz, CD_3CN): δ 12.6 (q, C-6), 104.6 (s, C-4), 111.5 (m, C-3), 150.5 (s, C-5) ppm. C-2 has not been detected.[S3]

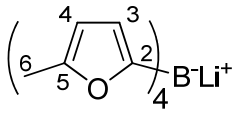
^{11}B NMR (128.3 MHz, CD_3CN): δ 1.9 (q, $J_{B\text{-}F}$ = 47.3 Hz) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ –141.9 (m) ppm.

NMR data for compound **1e** are in accordance with those reported in reference S3.

Lithium tetrakis(5-methyl-2-furyl)borate (1f)

To a preformed solution of 5-methylfuryl-2-lithium (22.5 mmol, 2.00 mL) in 40 mL of THF (see synthesis of compound **1d** for the lithiation of 2-methylfuran) was added dropwise $BF_3{\cdot}OEt_2$ (700 µL, 5.62 mmol) at 0 °C. The reaction mixture was stirred overnight at room temperature. The formed precipitate was separated by filtration and purified by two subsequent crystallisations from acetone/diethyl ether solutions to give **1f** as a yellowish solid (0.34 g, 51%).[S5]



Mp. 330-333 °C (decomposition).

^{1}H NMR (400 MHz, CD_3CN): δ 2.20 (s, 12 H, 6-H), 5.71-5.72 (m, 4 H, 4-H), 5.76-5.78 (m, 4 H, 3-H) ppm.

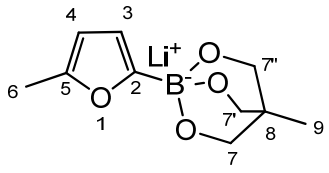
^{13}C NMR (100 MHz, CD_3CN): δ 14.4 (q, C-6), 112.8 (d, $J_{C\text{-}B}$ = 5.3 Hz, C-3), 106.2 (d, C-4), 150.3 (s, C-5), 176.8 (s, $J_{C\text{-}B}$ = 60.1 Hz, C-2) ppm.

^{11}B NMR (128.3 MHz, CD_3CN): δ 1.8 ppm.

HRMS (EI) *m*/*z* calcd. for $C_{20}H_{20}{}^{11}BO_4^-$: 335.1460, found 335.1466

Lithium 5-methyl-2-furanyl triol borate (1g)

The procedure described in reference S6 was used, starting from 2-methylfuran (1.00 mL, 11.0 mmol) and 1,1,1-tris(hydroxymethyl)ethane (1.32 g, 11.0 mmol). The crude product was purified by two subsequent crystallisations from acetonitrile/ethyl acetate solutions to give **1g** as a colorless solid (1.55 g, 68 %).



Mp. 124-126 °C (CH_3CN/EtOAc).

^{1}H NMR (400 MHz, DMSO + 1 drop of D_2O): δ 0.44 (s, 3 H, 9-H), 2.14 (s, 3 H, 6-H), 3.50 (s, 6 H, 7-H), 5.63-5.64 (m, 1 H, 4-H), 5.69-5.70 (m, 1 H, 3-H) ppm.

^{13}C NMR (100 MHz, DMSO + 1 drop of D_2O): δ 13.5 (q, C-6), 16.2 (q, C-9), 30.7 (s, C-8), 73.4 (t, C-7, C-7' and C-7''), 104.5 (d, C-4), 110.3 (d, C-3), 148.1 (s, C-5) ppm. C-2 has not been detected.

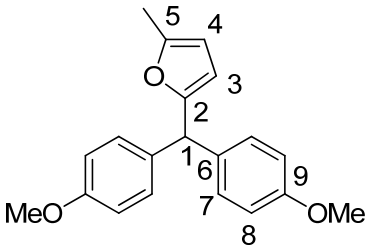
^{11}B NMR (128.3 MHz, CD_3CN): δ 0.5 ppm.

HRMS (EI) *m*/*z* calcd. for $C_{10}H_{14}{}^{11}BO_4^-$: 209.0991, found 209.0991.

3. Product studies

2-(Bis(4-methoxyphenyl)methyl)-5-methylfuran (3)

*From **1b** and **2a**-BF_4*: To a solution of **1b** (209 mg, 1.00 mmol) in acetonitrile (5 mL) was added dropwise a solution of **2a**-BF_4 (310 mg, 1.10 mmol) in acetonitrile (5 mL). The reaction mixture was stirred for 5 min at room temperature. The solvent was then evaporated under vacuum, and the residue was purified by flash chromatography on silica gel (ethyl acetate/*n*-pentane = 1/9) to yield **3** as a colorless oil (228 mg, 78%).



$\boldsymbol{R_f}$ = 0.76 (EtOAc/*n*-pentane = 1/4)

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.23 (s, 3 H, CH_3), 3.77 (s, 6 H, OCH_3), 5.28 (s, 1 H, 1-H), 5.70 (dd, J = 3.0, 0.5 Hz, 1 H, 3-H), 5.85 (dd, J = 3.0, 1.0 Hz, 1 H, 4-H), 6.81 (d, J = 8.8 Hz, 4 H, 7-H), 7.06 (d, J = 8.4 Hz, 4 H, 8-H) ppm.

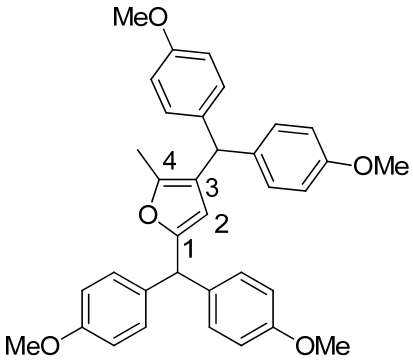
^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.9 (q, CH_3), 49.5 (d, C-1), 55.5 (q, OCH_3), 106.1 (d, C-4), 108.9 (d, C-3), 114.0 (d, C-8), 129.8 (d, C-7), 134.8 (s, C-6), 151.5 (s, C-9), 155.8 (s, C-5), 158.4 (s, C-2) ppm.

NMR data for compound **3** are in accord with those reported in reference S7.

*From **1c** and **2a**-BF_4*: To a solution of **1c** (210 mg, 1.00 mmol) in acetonitrile (5 mL) was added dropwise a solution of **2a**-BF_4 (310 mg, 1.10 mmol) in acetonitrile (5 mL). The reaction mixture was stirred for 5 min at room temperature. The solvent was then evaporated under vacuum, and the residue was purified by flash chromatography on silica gel (ethyl acetate/*n*-pentane = 1/9) to yield **3** as a colorless oil (170 mg, 55%). Spectroscopic data for **3** were the same as above.

*From **1d** and **2a**-BF_4*: To a solution of **1d** (237 mg, 1.00 mmol) in acetonitrile (5 mL) was added dropwise a solution of **2a**-BF_4 (310 mg, 1.10 mmol) in acetonitrile (5 mL). The reaction mixture was stirred for 5 min at room temperature. The solvent was then evaporated under vacuum, and the residue was purified by flash chromatography on silica gel (ethyl acetate/*n*-

pentane = 1/9) to give **3** and 3,5-bis(bis(4-methoxyphenyl)methyl)-2-methylfuran (**4**). For the crude product a 1/2-ratio of **3**/**4** was determined from the ^{1}H NMR spectrum. Isolated yield of **3**: 49 mg (16 %, spectroscopic data for **3** were the same as above); isolated yield of **4**: pale yellow oil, (106 mg, 34 %).



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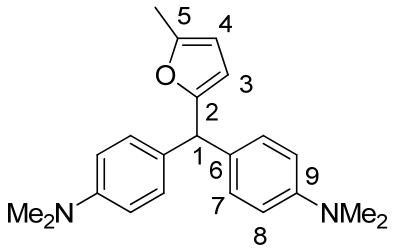
$\boldsymbol{R_f}$ = 0.49 (EtOAc/*n*-pentane = 1/4).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.01 (s, 3 H, CH_3), 3.76, 3.77 (2 s, 2 × 6H, OCH_3), 5.10 (s, 3-CH), 5.22 (s, 1-CH), 5.62 (s, 1 H, 2-H), 6.78-6.81 (m, 8 H, Ar), 7.01-7.06 (m, 8 H, Ar) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.2 (q, CH_3), 46.1 (d, 3-CH), 49.5 (d, 1-CH), 55.4 (q, OCH_3), 110.2 (d, C-2), 113.8 (d, Ar), 113.9 (d, Ar), 122.3 (s, C-3), 129.82 (d, Ar), 129.86 (d, Ar), 134.9 (s, Ar), 136.7 (s, Ar), 147.2 (s, C-4), 154.4 (s, C-1), 158.1 (s, Ar), 158.3 (s, Ar) ppm.

2-(Bis((4-dimethylamino)phenyl)methyl)-5-methylfuran (5)

*From **1e** and **2f**-BF_4*: To a deeply blue solution of **2f**-BF_4 (1.00 mmol, 340 mg) in acetonitrile (10 mL) was added dropwise a solution of **1e** (188 mg, 1.00 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 5 min while the blue color faded. The solvent was then evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (*n*-pentane/ethyl acetate = 9/1) to yield **5** as a colorless oil (294 mg, 88%).



$\boldsymbol{R_f}$ = 0.69 (EtOAc/*n*-pentane = 1/9)

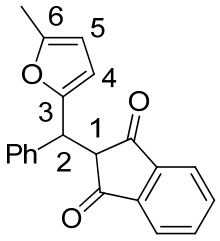
^{1}H NMR (400 MHz, CD_3CN): δ 2.23 (s, 3 H, CH_3), 2.90 (s, 12 H, 2 × NMe_2), 5.21 (s, 1 H, 1-H), 5.71 (d, *J* =1.8 Hz, 1 H, 3-H), 5.84 (d, *J* = 1.8 Hz, 1 H, 4-H), 6.67 (d, *J* = 8.8 Hz, 4 H, 7-H), 7.03 (d, *J* = 8.5 Hz, 4 H, 8-H) ppm.
^{13}C NMR (100 MHz, CD_3CN): δ 13.9 (q, Me), 41.0 (q, 2 × NMe_2). 49.3 (d, C-1), 106.0 (d, C-4), 108.5 (d, C-3), 112.9 (d, C-8), 129.5 (d, C-7), 131.2 (s, C-6), 149.5 (s, C-9), 151.2 (s, C-5), 156.7 (s, C-2) ppm.
HR-MS (ESI, positive): calc. for $C_{22}H_{26}N_2O$: 334.2045, found: 334.2045.

*From **1f** and **2f**-BF_4*: To a deeply blue solution of **2f**-BF_4 (1.00 mmol, 340 mg) in acetonitrile (10 mL) was added dropwise a solution of **1f** (342 mg, 1.00 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 5 min while the blue color faded. The solvent was then evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (*n*-pentane/ethyl acetate = 9/1) to yield **5** as a colorless oil (237 mg, 71%). Spectroscopic data for **5** were the same as above.

*From **1g** and **2f**-BF_4*: To a deeply blue solution of **2f**-BF_4 (1.00 mmol, 340 mg) in acetonitrile (10 mL) was added dropwise a solution of **1g** (216 mg, 1.00 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 5 min while the blue color faded. The solvent was then evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (*n*-pentane/ethyl acetate = 9/1) to yield **5** as a colorless oil (274 mg, 82%). Spectroscopic data for **5** were the same as above.

2-((5-Methylfuran-2-yl)(phenyl)methyl)-1H-indene-1,3(2H)-dione (14)

To an open flask charged with a mixture of **1e** (28 mg, 0.15 mmol) and 2-benzylidene-1H-indene-1,3(2H)-dione (**9**) (23.4 mg, 0.100 mmol) was added acetonitrile (2 mL) and methanol (0.5 mL). The mixture was stirred for 24 h at room temperature. After removing the solvents, the residue was purified by column chromatography on silica gel (EtOAc/*n*-pentane = 1/9) to yield **14** as a yellow oil (29 mg, 92%).



R_f = 0.3 (EtOAc/*n*-pentane = 1/9).

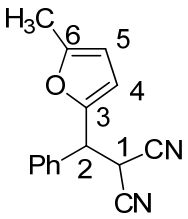
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 3 H, CH_3), 3.69 (d, J = 3.2 Hz, 1 H, 1-H), 4.96 (d, J = 2.9 Hz, 1 H, 2-H), 5.77-5.78 (m, 1 H, 5-H), 5.93-5.94 (m, 1 H, 4-H), 7.13-7.25 (m, 3 H, Ar, superimposed with $CHCl_3$), 7.35–7.38 (m, 2 H, Ar), 7.72–7.77 (m, 2 H, Ar), 7.86–7.90 (m, 2 H, Ar) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5 (q, CH_3), 44.2 (d, C-1), 57.6 (d, C-2), 106.3 (d, C-5), 109.0 (d, C-4), 106.4 (d, Ar), 109.1 (d, Ar), 123.2 (d, Ar), 123.3 (d, Ar), 127.5 (d, Ar), 128.6 (d, Ar), 129.4 (d, Ar), 135.6 (d, Ar), 138.7 (s, Ar), 142.6 (s, Ar), 142.9 (s, Ar), 151.2 (s, Ar), 152.3 (s, Ar), 198.9 (s, C=O), 199.0 (s, C=O) ppm.

HRMS (ESI): Calculated for [$C_{21}H_{15}O_3$] is 315.1027; obtained 315.1026.

2-((5-Methylfuran-2-yl)(phenyl)methyl) malononitrile (15)

To an open flask charged with a mixture of **1e** (28 mg, 0.15 mmol) and 2-benzylidenemalononitrile (**10**) (15.4 mg, 0.10 mmol) was added acetonitrile (2 mL) and methanol (0.5 mL). The mixture was stirred for 20 h at room temperature. After removing the solvents, the residue was purified by column chromatography on silica gel (EtOAc/*n*-pentane = 1/9) to yield **15** as a colorless oil (22 mg, 93%).



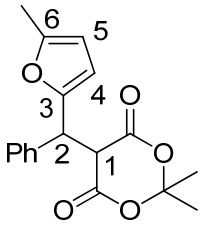
R_f = 0.25 (EtOAc/*n*-pentane = 1/19)

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.29 (s, 3 H, CH_3), 4.40 (d, J = 7.4 Hz, 1 H, 1-H), 4.55 (d, J = 7.4 Hz, 1 H, 2-H), 5.94–5.95 (m, 1 H, 5-H), 6.19–6.20 (m, 1 H, 4-H), 7.37–7.44 (m, 5 H, Ar) ppm.

^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.8 (q, CH_3), 29.1 (d, C-1), 46.5 (d, C-2), 107.0 (d, C-5), 110.6 (d, C-4), 111.70 (s, C≡N), 111.74 (s, C≡N), 128.5 (d, Ar), 129.4 (d, Ar), 129.5 (d, Ar), 135.2 (s, Ar), 147.6 (s, C-3), 153.5 (s, C-6) ppm.

2,2-Dimethyl-5-((5-methylfuran-2-yl)(phenyl)methyl)-1,3-dioxane-4,6-dione (16)

To an open flask charged with a mixture of **1e** (28.2 mg, 0.150 mmol) and 5-benzylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (**11**) (23.2 mg, 0.100 mmol) was added CH_3CN (2 mL) and CH_3OH (0.5 mL). The mixture was allowed to stir for 24 h at room temperature. After removing the solvent, the residue was purified by column chromatography on silica gel (EtOAc/*n*-pentane = 1/4) to yield **16** as an off-white powder (27 mg, 86%).



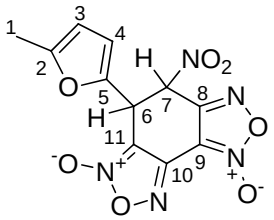
$\boldsymbol{R_f}$ = 0.07 (EtOAc/*n*-pentane = 1/9)

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.47 (s, 3 H, CH_3), 1.71 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 4.21 (d, J = 3.1 Hz, 1 H, 1-H), 5.22 (d, J = 2.7 Hz, 1 H, 2-H), 5.88-5.93 (m, 2 H, 5-H and 4-H), 7.27-7.34 (m, 3 H, Ar), 7.42-7.46 (m, 2 H, Ar) ppm.

^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.7 (q, CH_3), 28.1 (q, CH_3), 28.4 (q, CH_3), 44.6 (d, C-1), 50.7 (d, C-2), 105.3 (s, $\underline{C}(CH_3)_2$), 106.8 (d, C-4 or C-5), 109.1 (d, C-4 or C-5), 128.2 (d, Ar), 128.8 (d, Ar), 129.9 (d, Ar), 137.7 (s, Ar), 151.2 (s, C-3 or C-6), 151.3 (s, C-3 or C-6), 164.4 (s, C=O), 164.6 (s, C=O) ppm.

2-Methyl-5-(4-nitrobenzodifuroxanyl)furan (17)

In an NMR tube **12** (15 mg, 0.063 mmol) and **1e** (12 mg, 0.063 mmol) were mixed in CD_3CN (1 mL) at room temperature. After 5 min a drop of H_2O was added. Then the NMR spectra were recorded to characterise **17**. Attempts to isolate **17** failed.

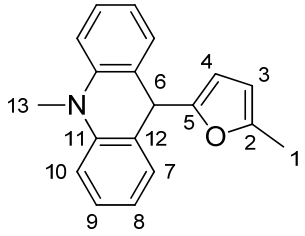


^{1}H NMR (400 MHz, CD_3CN): δ 2.19 (s, 3 H, CH_3), 5.52 (m, 1 H, 6-H), 5.99 (m, 1 H, 4-H), 6.31 (m, 1 H, 3-H), 6.53 (m, 1 H, 7-H) ppm.

^{13}C NMR (100 MHz, CD_3CN): δ 12.5 (q, CH_3), 34.9 (d, C-6), 78.1 (d, C-7), 106.9 (d, C-4), 111.3 (d, C-3), 121.6 (s, C-10 or C-11), 152.7 and 152.9 (s, C-1 and C-5) ppm. C-8, C-9, C-10, and C-11 have not been detected.

10-Methyl-9-(5-methylfuran-2-yl)-4a,9,9a,10-tetrahydroacridine (18)

A solution of *N*-methylacridinium tetrafluoroborate **13** (281 mg, 1.00 mmol) in acetonitrile (5 mL) was prepared. At 20 °C, a solution of trifluoroborate **1e** (188 mg, 1.00 mmol) was added dropwise. After 1 h the reaction was complete. Then the solvent was removed in vacuum. The crude product was purified by chromatography on silica gel (*n*-pentane/AcOEt = 9/1) to yield **18** (yellow oil, 250 mg, 92 %).



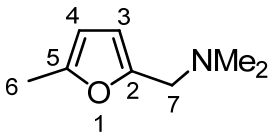
R_f = 0.85 (*n*-pentane/AcOEt = 9/1).

^{1}H NMR (400 MHz, CD_3CN): δ 2.23 (s, 3 H, Me), 3.42 (s, 3 H, NMe), 5.24 (s, 1 H, 6-H), 5.52 (m, 1 H, 3-H), 5.78 (1 H, 4-H), 6.90-6.98 (m, 4 H, 8-H and 10-H) and 7.18–7.30 (m, 4 H, 7-H and 9-H) ppm.

^{13}C NMR (100 MHz, CD_3CN): δ 13.7 (C-1), 33.1 (C-13), 42.6 (C-6), 105.9 (d, C-4), 106.8 (d, C-3), 111.9 (d, Ar), 112.3 (d, Ar), 120.5 (d, Ar), 124.2 (q, Ar), 126.9 (q, Ar), 127.5 (d, Ar) 128.7 (d, Ar), 142.5 (q, Ar), 143.6 (q, Ar), 151.3 and 154.4 (C-2 and C-5) ppm.

N,N-Dimethyl-1-(5-methylfuran-2-yl)methanamine (20)

The organoboron compound **1b,d,e,g** (1.1 mmol) was added to a solution of the iminium salt **19-X**$^-$ (1.0 mmol) in acetontrile (10 mL). After stirring at r.t. for 1 h, the reaction was quenched by adding a few drops of an aqeous saturated NH_4Cl solution. The resulting mixture was washed with brine (10 mL), and the aqueous phase was extracted with ethyl acetate (2 × 10 mL). Combining the organic phases, drying ($MgSO_4$) and evaporating the volatile components gave the disubstituted furan **20** as a pale liquid (yields of **20**: (a) 120 mg, 88 %, from the reaction of **1b** with **19**-$CF_3CO_2^-$; (b) 130 mg, 93 % from the reaction of **1e** with **19**-$CF_3CO_2^-$; (c) yields of further reactions (see Scheme 4 of the main text) were calculated from the crude ^{1}H NMR spectra.)



^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 6 H, NMe_2), 2.30 (s, 3 H, Me), 3.43 (s, 2 H, 7-H), 5.91 (m, 1 H, 3-H), 6.08 (m, 1 H, 4-H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6 (C-6), 44.9 (NMe_2), 55.9 (C-7), 105.83 (C-4), 109.4 (C-3), 150.2 (C-2), 151.92 (C-5) ppm.

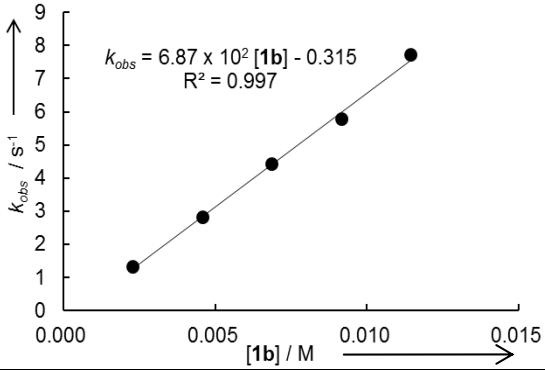
4. Kinetics

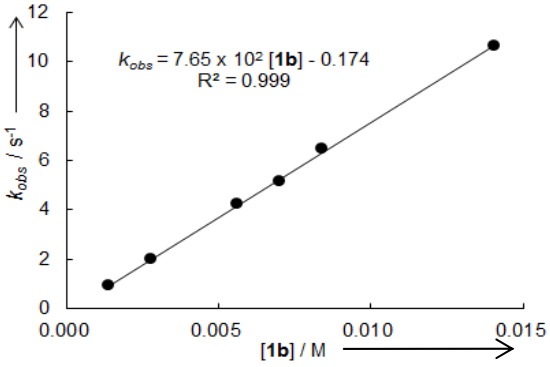
4.1 Kinetics of the reactions of 1b–g with benzhydrylium ions 2a–j ($Ar_2CH^+X^-$)

The rates of the reactions of **1b–g** with the benzhydrylium ions **2a–j** ($Ar_2CH^+X^-$) were measured photometrically, by using diode array detector or conventional stopped flow technique as described previously (Ref. S1) at 20 °C in dry CH_3CN.

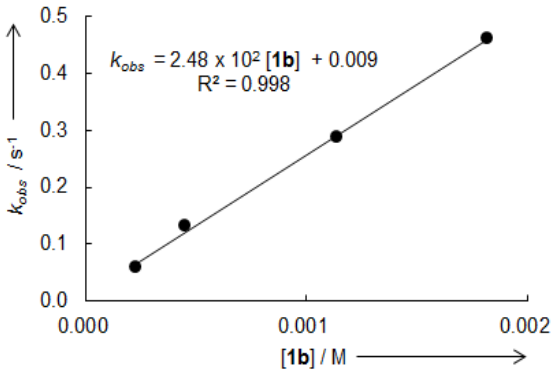
First-order rate constants k_{obs} were obtained by least-squares fitting of the absorbances to the mono-exponential curve $A_t = A_0 \exp(-k_{obs}t) + C$. Since $k_{obs} = k_2[Nu]$, the second-order rate constants k (M^{-1} s^{-1}) were derived from the slopes of the linear plots of k_{obs} (s^{-1}) vs. [Nu].

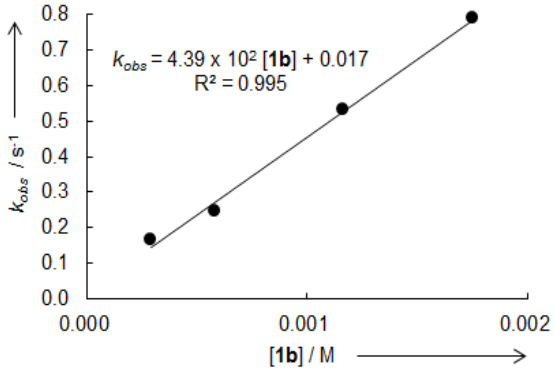
Supplementary Table S1. Kinetics of the reactions of **1b** with $Ar_2CH^+X^-$ **2a** and **2b** in CH_3CN at 20°C

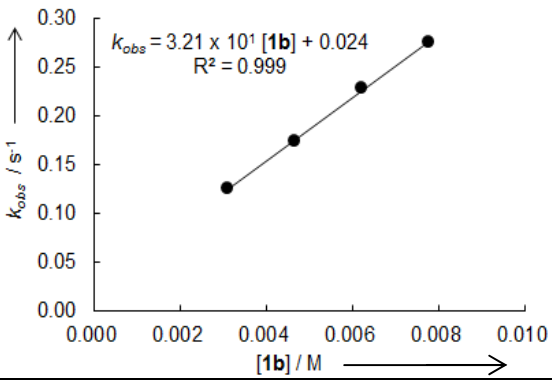
[**2a**-BF_4^-] / M	[**1b**] / M	k_{obs} / s^{-1}	λ = 500 nm	k_2 / M^{-1} s^{-1}
4.1×10^{-5}	2.29×10^{-3}	1.31		6.87×10^2
	4.58×10^{-3}	2.83		
	6.87×10^{-3}	4.36		
	9.16×10^{-3}	5.72		
	1.15×10^{-2}	7.76		

[**2a**-BF_4^-] / M	[**1b**] / M	k_{obs} / s^{-1}	(in CH_2Cl_2) λ = 500 nm	k_2 / M^{-1} s^{-1}
4.1×10^{-5}	1.41×10^{-3}	9.04×10^{-1}		7.65×10^2
	2.81×10^{-3}	2.00		
	5.62×10^{-3}	4.21		
	7.03×10^{-3}	5.14		
	8.44×10^{-3}	6.45		
	1.41×10^{-2}	1.06×10^1		

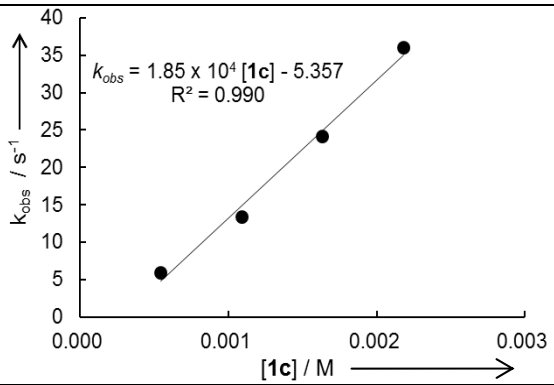
Supplementary Table S1. (Continued)

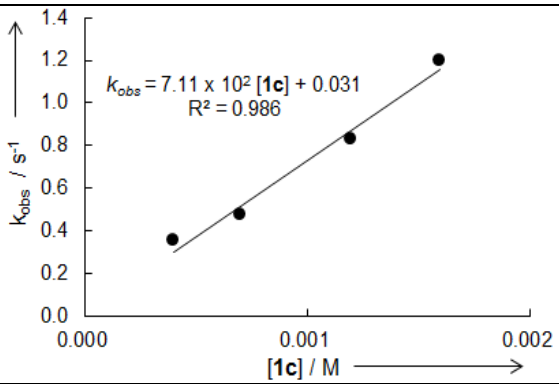
[**2a**-$SbCl_6^-$] / M	[**1b**] / M	k_{obs} / s^{-1}	λ = 500 nm	k_2 / M^{-1} s^{-1}
1.2×10^{-5}	2.28×10^{-4}	5.78×10^{-2}		2.48×10^{2}
	4.56×10^{-4}	1.31×10^{-1}		
	1.14×10^{-3}	2.86×10^{-1}		
	1.82×10^{-3}	4.60×10^{-1}		

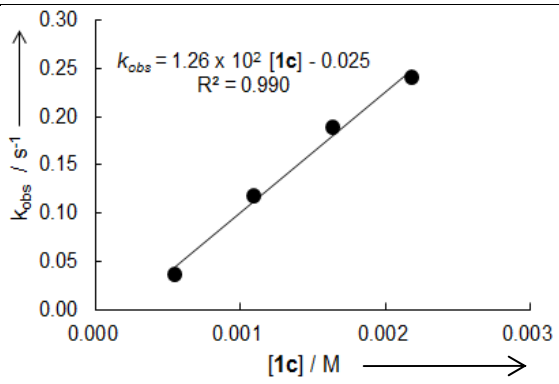
[**2a**-PF_6^-] / M	[**1b**] / M]	k_{obs} / s^{-1}	λ = 500 nm	k_2 / M^{-1} s^{-1}
1.2×10^{-5}	2.92×10^{-4}	1.65×10^{-1}		4.39×10^{2}
	5.84×10^{-4}	2.46×10^{-1}		
	1.17×10^{-3}	5.34×10^{-1}		
	1.75×10^{-3}	7.88×10^{-1}		

[**2b**-BF_4^-] / M	[**1b**] / M	k_{obs} / s^{-1}	λ = 524 nm	k_2 / M^{-1} s^{-1}
5.8×10^{-5}	3.11×10^{-3}	1.25×10^{-1}		3.21×10^{1}
	4.67×10^{-3}	1.74×10^{-1}		
	6.23×10^{-3}	2.28×10^{-1}		
	7.79×10^{-3}	2.74×10^{-1}		

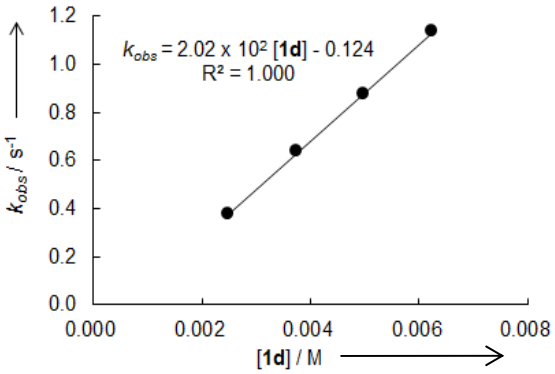
Supplementary Table S2. Kinetics of the reactions of **1c** with $Ar_2CH^+BF_4^-$ **2b-d** in CH_3CN at 20°C

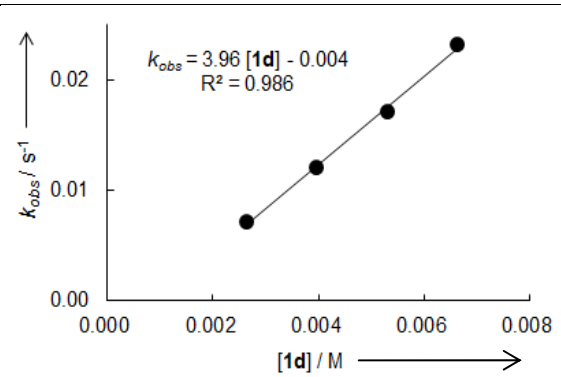
[**2b**] / M	[**1c**] / M	k_{obs} / s^{-1}	λ = 524 nm	k_2 / M^{-1} s^{-1}
5.2×10^{-5}	5.46×10^{-4}	5.93		1.85×10^4
	1.09×10^{-3}	1.34×10^1		
	1.64×10^{-3}	2.42×10^1		
	2.18×10^{-3}	3.59×10^1		

[**2c**] / M	[**1c**] / M	k_{obs} / s^{-1}	λ = 592 nm	k_2 / M^{-1} s^{-1}
3.6×10^{-5}	3.99×10^{-4}	3.52×10^{-1}		7.11×10^2
	6.98×10^{-4}	4.74×10^{-1}		
	1.20×10^{-3}	8.26×10^{-1}		
	1.60×10^{-3}	1.20		

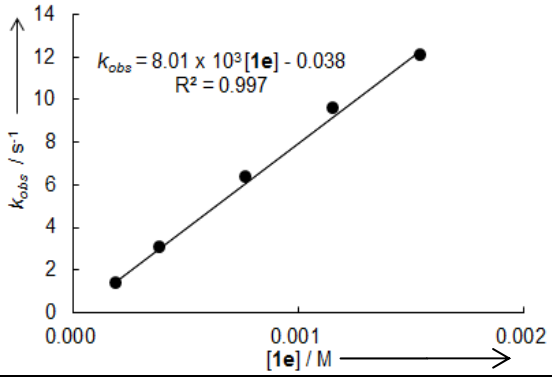
[**2d**] / M	[**1c**] / M	k_{obs} / s^{-1}	λ = 586 nm	k_2 / M^{-1} s^{-1}
3.9×10^{-5}	5.46×10^{-4}	3.60×10^{-2}		1.26×10^2
	1.09×10^{-3}	1.18×10^{-1}		
	1.64×10^{-3}	1.89×10^{-1}		
	2.18×10^{-3}	2.41×10^{-1}		

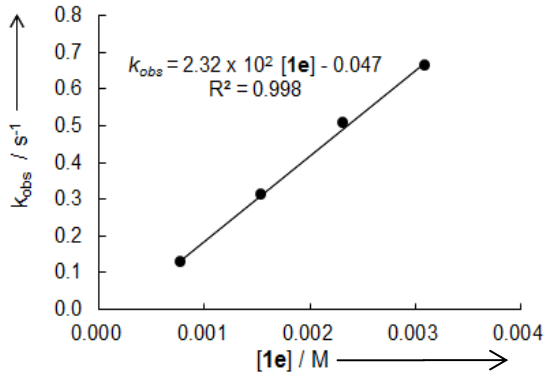
Supplementary Table S3. Kinetics of the reactions of **1d** with $Ar_2CH^+BF_4^-$ **2a** and **2b** in CH_3CN at 20°C

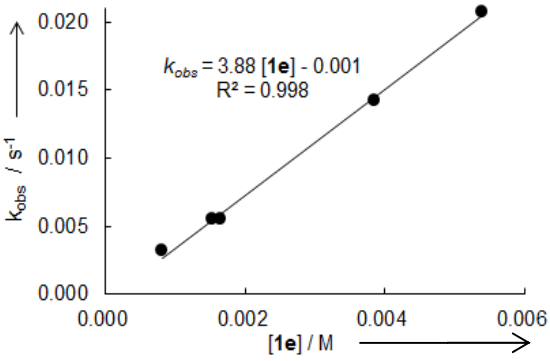
[**2a**] / M	[**1d**] / M	k_{obs} / s^{-1}	λ = 500 nm	k_2 / M^{-1} s^{-1}
4.0×10^{-5}	2.50×10^{-3}	3.78×10^{-1}		2.02×10^2
	3.74×10^{-3}	6.36×10^{-1}		
	4.99×10^{-3}	8.75×10^{-1}		
	6.24×10^{-3}	1.14		

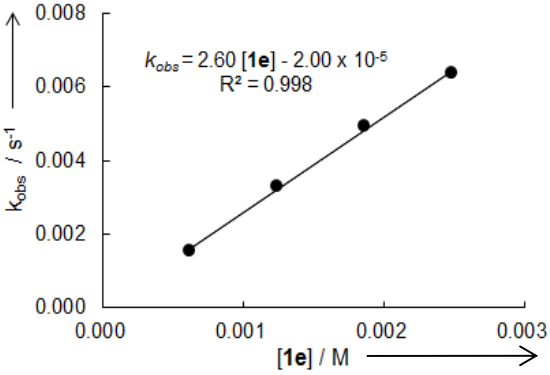
[**2b**] / M	[**1d**] / M	k_{obs} / s^{-1}	λ = 524 nm	k_2 / M^{-1} s^{-1}
5.1×10^{-5}	2.65×10^{-3}	7.12×10^{-3}		3.96
	3.97×10^{-3}	1.21×10^{-2}		
	5.29×10^{-3}	1.61×10^{-2}		
	6.61×10^{-3}	2.32×10^{-2}		

Supplementary Table S4. Kinetics of the Reactions of **1e** with $Ar_2CH^+X^-$ **2d-f** in CH_3CN at 20°C

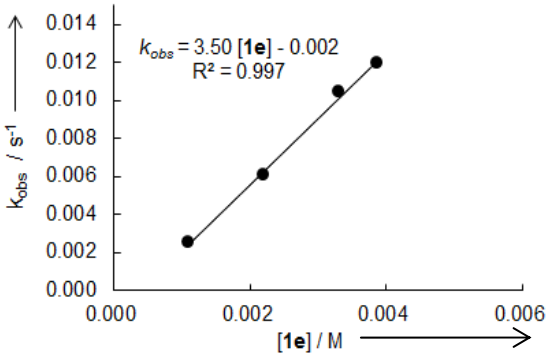
[**2d**-BF_4^-] / M	[**1e**] / M	k_{obs} / s^{-1}	λ = 586 nm	k_2 / M^{-1} s^{-1}
2.2×10^{-5}	1.93×10^{-4}	1.34		8.01×10^3
	3.86×10^{-4}	3.01		
	7.72×10^{-4}	6.34		
	1.16×10^{-3}	9.56		
	1.54×10^{-3}	1.20×10^1		

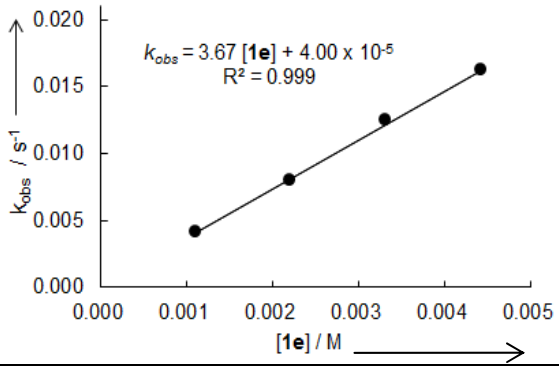
[**2e**-BF_4^-] / M	[**1e**] / M	k_{obs} / s^{-1}	λ = 610 nm	k_2 / M^{-1} s^{-1}
2.4×10^{-5}	7.72×10^{-4}	1.28×10^{-1}		2.32×10^2
	1.54×10^{-3}	3.14×10^{-1}		
	2.32×10^{-3}	5.06×10^{-1}		
	3.09×10^{-3}	6.62×10^{-1}		

[**2f**-BF_4^-] / M	[**1e**] / M	k_{obs} / s^{-1}	λ = 607 nm	k_2 / M^{-1} s^{-1}
2.8×10^{-5}	8.27×10^{-4}	3.16×10^{-3}		3.88
	1.54×10^{-3}	5.45×10^{-3}		
	1.65×10^{-3}	5.48×10^{-3}		
	3.86×10^{-3}	1.42×10^{-2}		
	5.41×10^{-3}	2.07×10^{-2}		

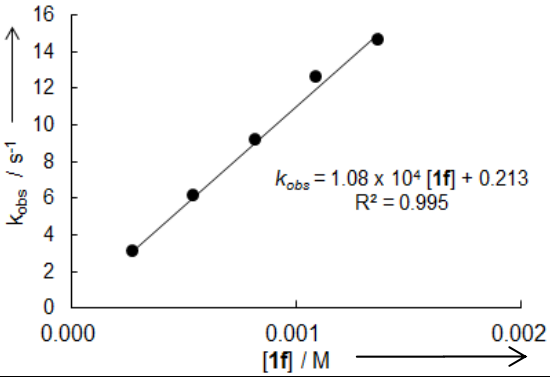
[**2f**-BF_4^-] / M	[**1e**] / M	k_{obs} / s^{-1}	(with 1 equivalent of 18-crown-6) λ = 607 nm	k_2 / M^{-1} s^{-1}
2.8×10^{-5}	6.22×10^{-4}	1.51×10^{-3}		2.60
	1.24×10^{-3}	3.30×10^{-3}		
	1.87×10^{-3}	4.92×10^{-3}		
	2.49×10^{-3}	6.36×10^{-3}		

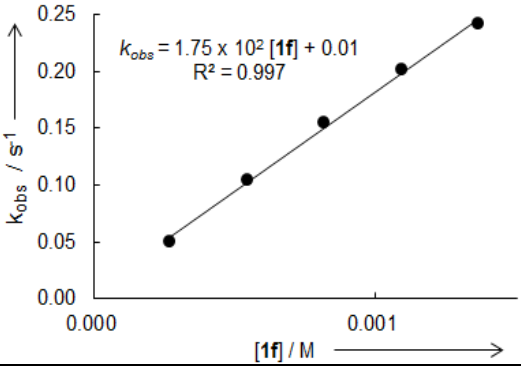
Supplementary Table S4. (Continued)

[**2f**-OTf$^-$] / M	[**1e**] / M	k_{obs} / s^{-1}	λ = 607 nm	k_2 / M^{-1} s^{-1}
2.8×10^{-5}	1.11×10^{-3}	2.51×10^{-3}		3.50
	2.21×10^{-3}	6.01×10^{-3}		
	3.32×10^{-3}	1.05×10^{-2}		
	3.87×10^{-3}	1.20×10^{-2}		

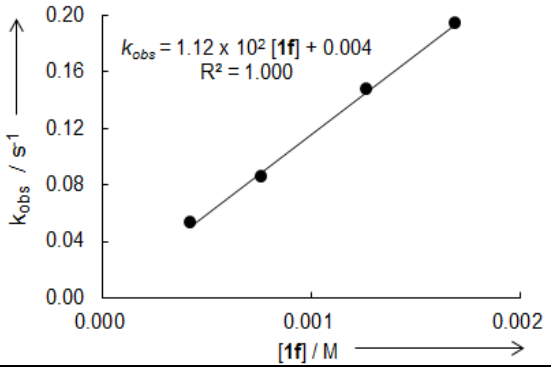
[**2f**-Br$^-$] / M	[**1e**] / M	k_{obs} / s^{-1}	λ = 607 nm	k_2 / M^{-1} s^{-1}
2.8×10^{-5}	1.11×10^{-3}	4.13×10^{-3}		3.67
	2.21×10^{-3}	7.99×10^{-3}		
	3.32×10^{-3}	1.24×10^{-2}		
	4.43×10^{-3}	1.62×10^{-2}		

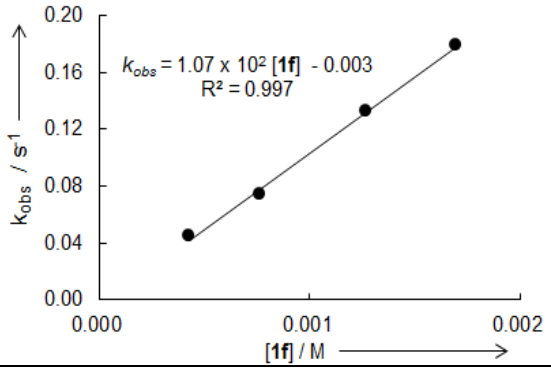
Supplementary Table S5. Kinetics of the reactions of **1f** with $Ar_2CH^+X^-$ **2e-g** in CH_3CN at 20°C

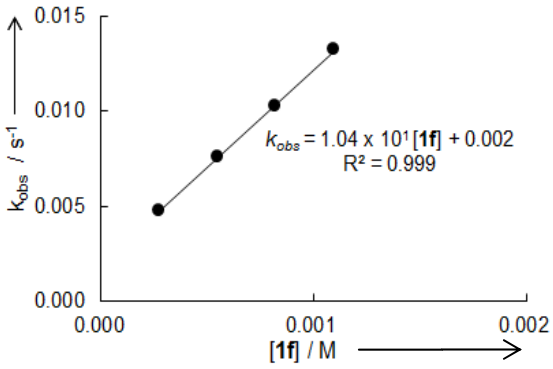
[**2e**-BF_4^-] / M	[**1f**] / M	k_{obs} / s^{-1}	λ = 586 nm	k_2 / M^{-1} s^{-1}
2.2×10^{-5}	2.73×10^{-4}	3.05		1.08×10^4
	5.47×10^{-4}	6.08		
	8.20×10^{-4}	9.11		
	1.09×10^{-3}	1.26×10^1		
	1.37×10^{-3}	1.46×10^1		

[**2f**-BF_4^-] / M	[**1f**] / M	k_{obs} / s^{-1}	λ = 607 nm	k_2 / M^{-1} s^{-1}
2.8×10^{-5}	2.73×10^{-4}	5.01×10^{-2}		1.75×10^2
	5.47×10^{-4}	1.04×10^{-1}		
	8.20×10^{-4}	1.54×10^{-1}		
	1.09×10^{-3}	2.01×10^{-1}		
	1.37×10^{-3}	2.41×10^{-1}		

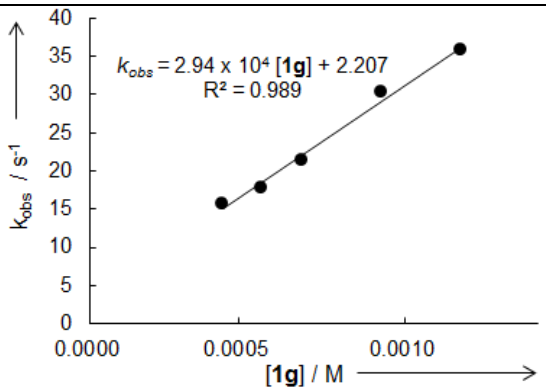
Supplementary Table S5. (Continued)

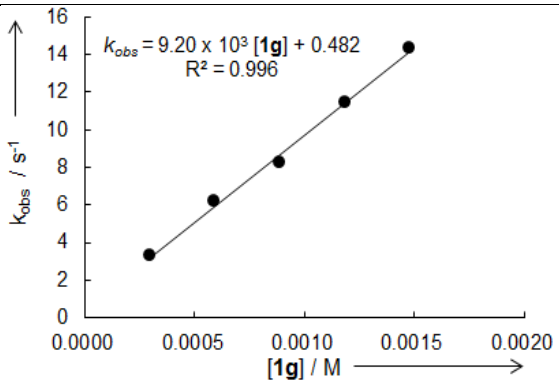
[**2f**-PF_6^-] / M	[**1f**] / M	k_{obs} / s^{-1}	λ = 607 nm	k_2 / M^{-1} s^{-1}
2.8×10^{-5}	4.24×10^{-4}	5.31×10^{-2}		1.12×10^{2}
	7.63×10^{-4}	8.49×10^{-2}		
	1.27×10^{-3}	1.47×10^{-1}		
	1.70×10^{-3}	1.94×10^{-1}		

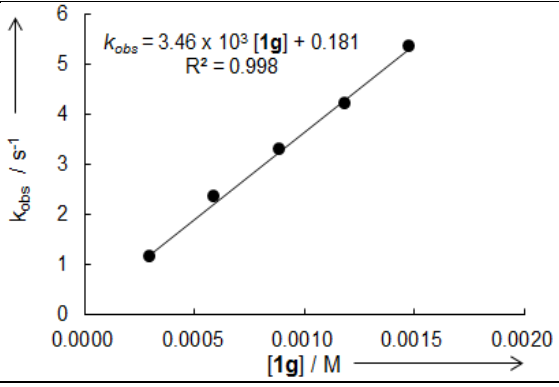
[**2f**-OTf^-] / M	[**1f**] / M	k_{obs} / s^{-1}	λ = 607 nm	k_2 / M^{-1} s^{-1}
2.8×10^{-5}	4.24×10^{-4}	4.49×10^{-2}		1.07×10^{2}
	7.63×10^{-4}	7.39×10^{-2}		
	1.27×10^{-3}	1.32×10^{-1}		
	1.70×10^{-3}	1.79×10^{-1}		

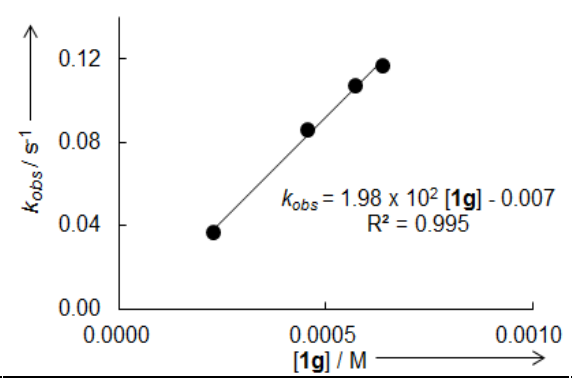
[**2h**-BF_4^-] / M	[**1f**] / M	k_{obs} / s^{-1}	λ = 610 nm	k_2 / M^{-1} s^{-1}
2.4×10^{-5}	2.73×10^{-4}	4.76×10^{-3}		1.04×10^{1}
	5.47×10^{-4}	7.58×10^{-3}		
	8.20×10^{-4}	1.02×10^{-2}		
	1.09×10^{-3}	1.33×10^{-2}		

Supplementary Table S6. Kinetics of the reactions of **1g** with $Ar_2CH^+BF_4^-$ **2g-j** in CH_3CN at 20 °C.

[**2g**] / M	[**1g**] / M	k_{obs} / s^{-1}	λ = 620 nm	k_2 / M^{-1} s^{-1}
1.4×10^{-5}	4.82×10^{-4}	17.0		2.94×10^4
	6.02×10^{-4}	19.1		
	7.22×10^{-4}	22.6		
	9.63×10^{-4}	31.6		
	1.20×10^{-3}	37.0		

[**2h**] / M	[**1g**] / M	k_{obs} / s^{-1}	λ = 620 nm	k_2 / M^{-1} s^{-1}
1.6×10^{-5}	2.96×10^{-4}	3.25		9.20×10^3
	5.93×10^{-4}	6.21		
	8.89×10^{-4}	8.25		
	1.19×10^{-3}	11.4		
	1.48×10^{-3}	14.3		

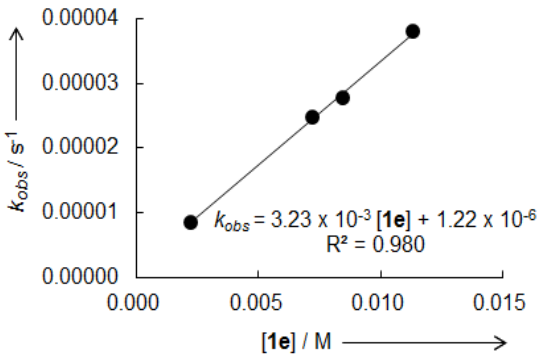
[**2i**] / M	[**1g**] / M	k_{obs} / s^{-1}	λ = 620 nm	k_2 / M^{-1} s^{-1}
1.4×10^{-5}	2.96×10^{-4}	1.14		3.46×10^3
	5.93×10^{-4}	2.33		
	8.89×10^{-4}	3.27		
	1.19×10^{-3}	4.21		
	1.48×10^{-3}	5.33		

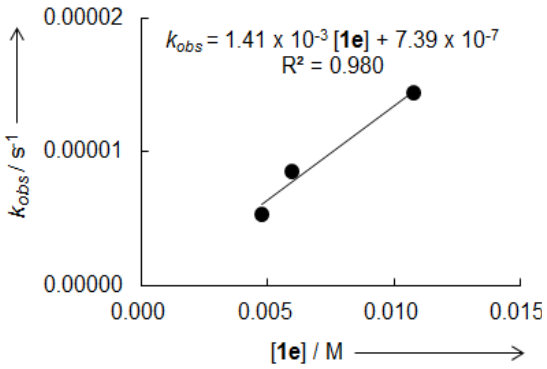
[**2j**] / M	[**1g**] / M	k_{obs} / s^{-1}	λ = 620 nm	k_2 / M^{-1} s^{-1}
1.4×10^{-5}	2.28×10^{-4}	3.66×10^{-2}		1.98×10^2
	4.56×10^{-4}	8.62×10^{-2}		
	5.70×10^{-4}	1.07×10^{-1}		
	6.38×10^{-4}	1.17×10^{-1}		

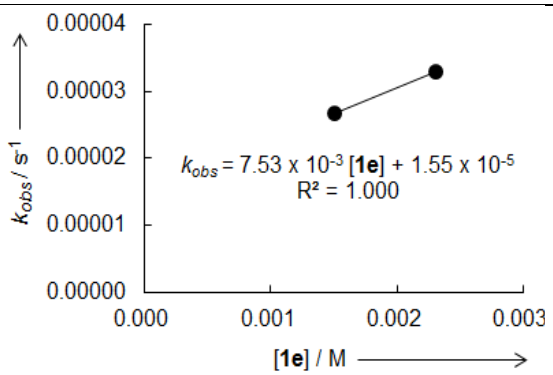
4.2 Kinetics of the reactions of 1e with Michael acceptors 9–13

The rates of the reaction of **1e** with Michael acceptors **9**–**13** were measured photometrically, under pseudo-first order conditions (excess of **1e**) at the absorption maxima of **9-13** by UV-Vis spectrometers (using diode array detector at 20 ^{o}C). First-order rate constants k_{obs} were obtained by least-squares fitting of the absorbances either to the mono-exponential curve $A_t = A_0 \exp(-k_{obs}t) + C$ (exponential decrease) or to $A_t = A_0[1 - \exp(1 - k_{obs}t)] + C$ (mono-exponential increase). Since $k_{obs} = k_2[Nu]$, the second-order rate constants k_2 (M^{-1} s^{-1}) were derived from the slopes of the linear plots of k_{obs} (s^{-1}) vs. [Nu].

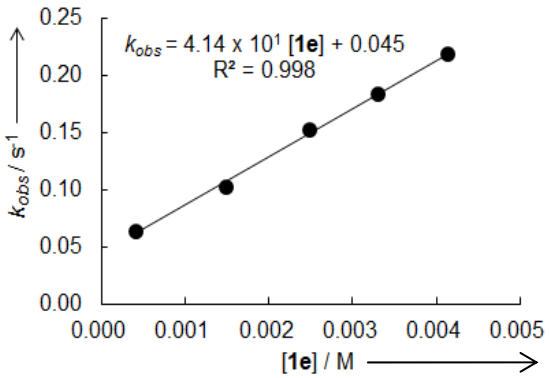
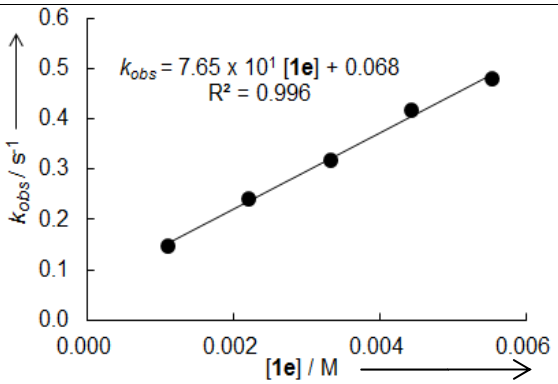
Supplementary Table S7. Kinetics of the reactions of **1e** with **9-11** in CH_3CN/MeOH (95:5).

[**9**] / M	[**1e**] / M	k_{obs} / s^{-1}	λ = 340 nm	k_2 / M^{-1} s^{-1}
4.93×10^{-5}	2.21×10^{-3}	8.52×10^{-6}		3.23×10^{-3}
4.43×10^{-5}	7.21×10^{-3}	2.48×10^{-5}		
4.52×10^{-5}	8.46×10^{-3}	2.78×10^{-5}		
4.56×10^{-5}	1.13×10^{-2}	3.81×10^{-5}		

[**10**] / M	[**1e**] / M	k_{obs} / s^{-1}	λ = 306 nm	k_2 / M^{-1} s^{-1}
4.72×10^{-5}	4.79×10^{-3}	5.36×10^{-6}		1.41×10^{-3}
4.68×10^{-5}	5.94×10^{-3}	8.58×10^{-6}		
4.64×10^{-5}	1.08×10^{-2}	1.44×10^{-5}		

[**11**] / M	[**1e**] / M	k_{obs} / s^{-1}	λ = 306 nm	k_2 / M^{-1} s^{-1}
4.97×10^{-5}	1.50×10^{-3}	2.68×10^{-5}		7.53×10^{-3}
4.90×10^{4}	2.31×10^{-3}	3.29×10^{-5}		

Supplementary Table S8. Kinetics of the Reactions of **1e** with **12–13** in CH_3CN.

[**12**] / M	[**1e**] / M	k_{obs} / s^{-1}	Increase at λ = 395 nm	k_2 / M^{-1} s^{-1}
6.1×10^{-4}	4.14×10^{-4}	6.47×10^{-2}		4.14×10^{1}
	1.49×10^{-3}	1.04×10^{-1}		
	2.48×10^{-3}	1.57×10^{-1}		
	3.31×10^{-3}	1.83×10^{-1}		
	4.14×10^{-3}	2.17×10^{-1}		
[**13**] / M	[**1e**] / M	k_{obs} / s^{-1}	λ = 415 nm	k_2 / M^{-1} s^{-1}
4.1×10^{-4}	1.11×10^{-3}	1.46×10^{-1}		7.65×10^{1}
	2.21×10^{-3}	2.42×10^{-1}		
	3.32×10^{-3}	3.18×10^{-1}		
	4.43×10^{-3}	4.17×10^{-1}		
	5.53×10^{-3}	4.80×10^{-1}		

5. Determination of the nucleophilicity of organoboron compounds 1b–g

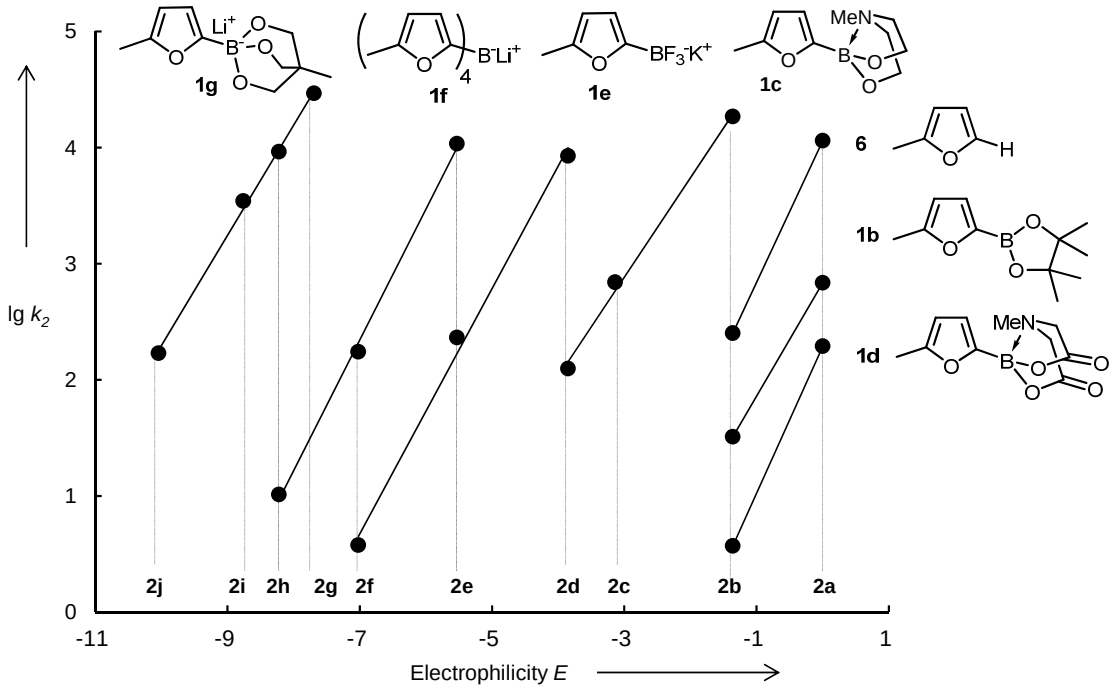


Figure S1. Plots of the logarithm of the second-order rate constants log k_2 versus the electrophilicity parameters E used for the determination of the nucleophilicity N and sensitivity (slope) parameters s_N (see equation (1) and Table 1 in the main text).

Supplementary Table S8. Determination of the nucleophilicity of **1b**–**g**.

Nucleophiles	s_N (slopes)	N	R^2
1b	0.98	2.90	-
1c	0.86	6.38	-
1d	1.26	1.84	0.997
1e	1.04	7.66	0.994
1f	1.12	9.09	0.998
1g	0.92	12.55	0.999

6. References

S1. H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R. Loos, A. R. Ofial, G. Remennikov and H. Schimmel, *J. Am. Chem. Soc*., 2001, **123**, 9500.

S2. D. Florentin, M. C. Fournié-Zaluski, M. B Callanquin and P. Roques, *J. Heterocycl. Chem*., 1976, **13**, 1265.

S3. D. M. Knapp, E. P. Gillis and M. D. Burke, *Org. Lett.,* 2010, **12**, 2314.

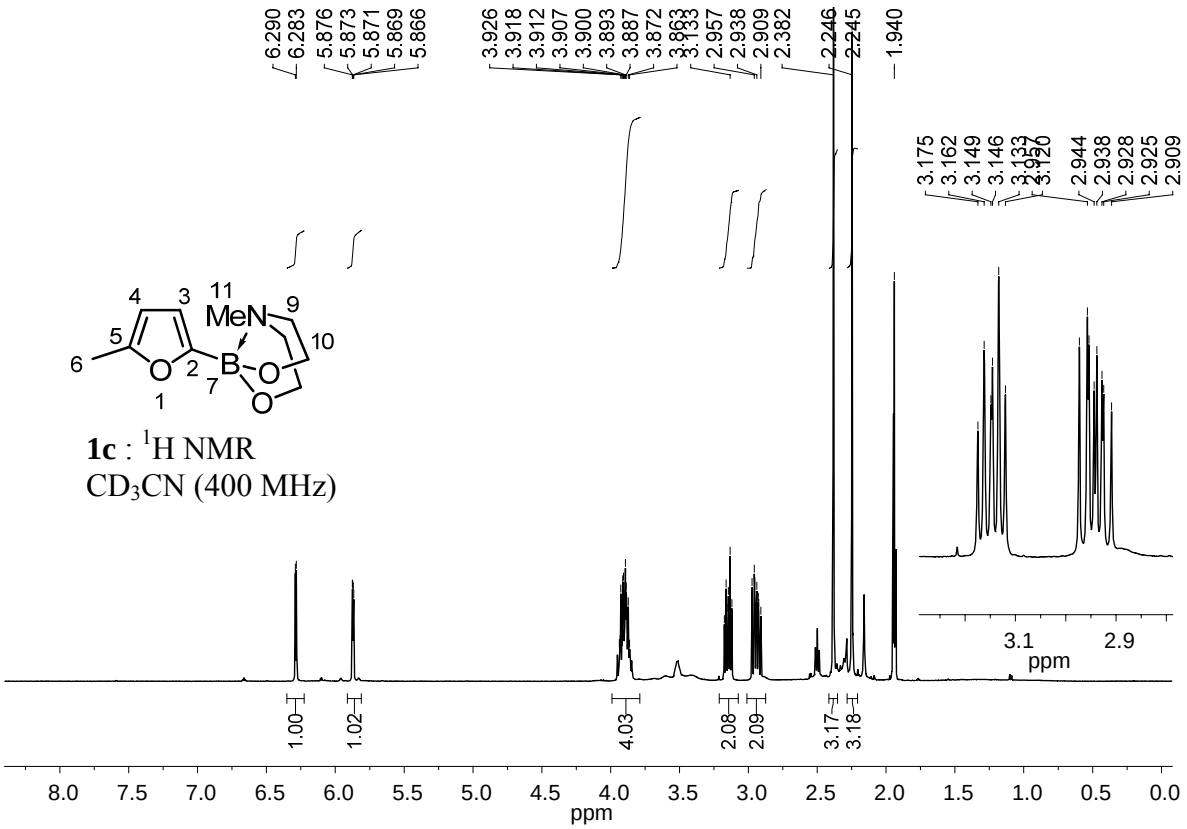
S4. G. A. Molander, B. Canturk and L. E. Kennedy, *J. Org. Chem,.* 2009, **74**, 973.

S5. For an early synthesis of potassium tetrakis(5-methyl-2-furyl)borate, see: A. N. Nesmeyanov, V. A. Sazonova and V. N. Drozd,. *Russ. Chem. Bull.,* 1959, **8**, 147.

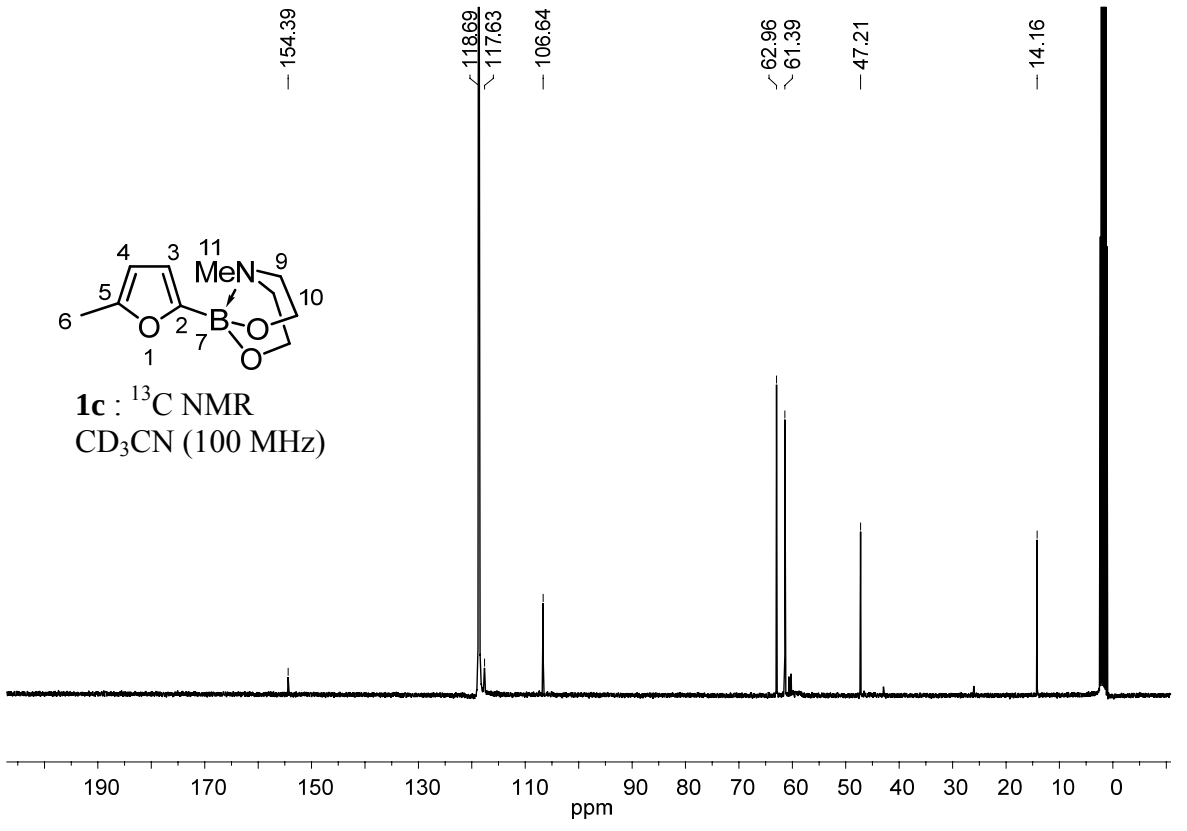
S6. X.-Q, Yu, T. Shirai, Y. Yamamoto and N. Miyaura. *Chem. Asian. J*., 2011, **6**, 932.

S7. M. Hofmann, N. Hampel, T. Kanzian and H. Mayr, *Angew. Chem. Int. Ed,.* 2001, **43**, 5402.

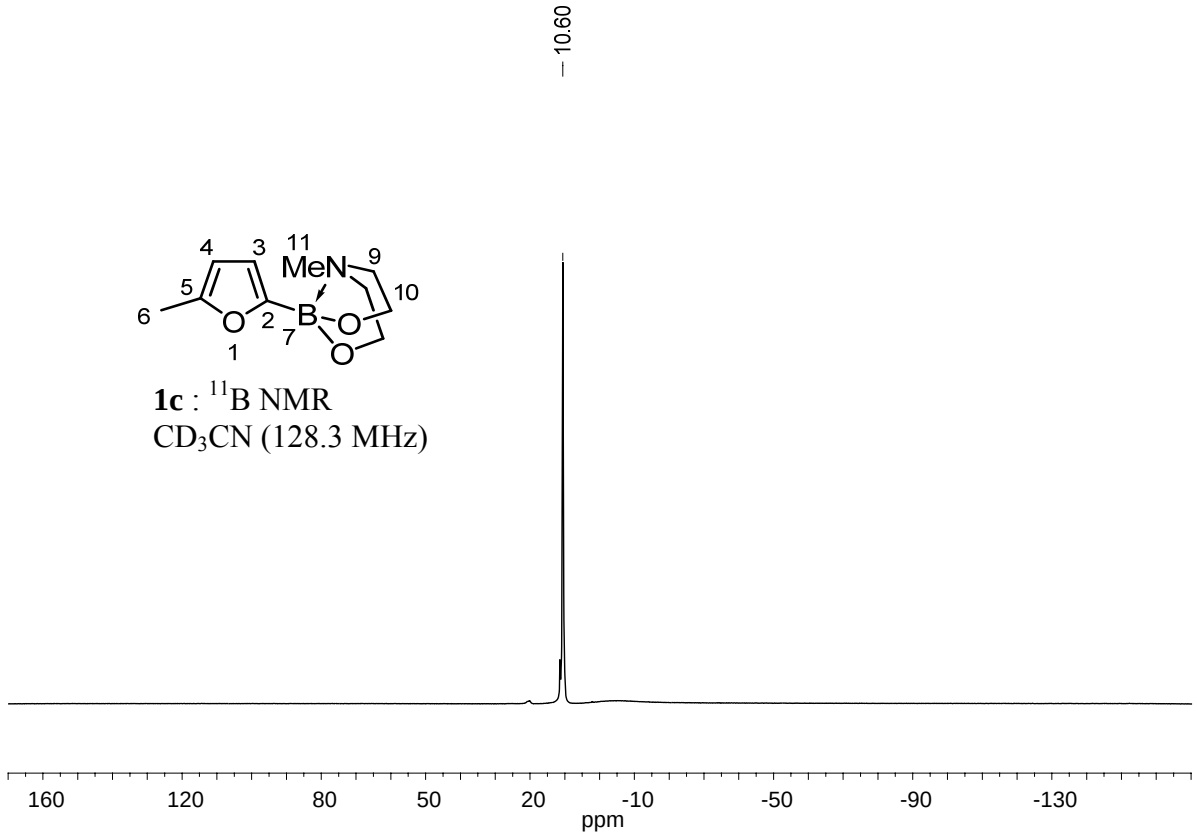
7. Copies of NMR Spectra



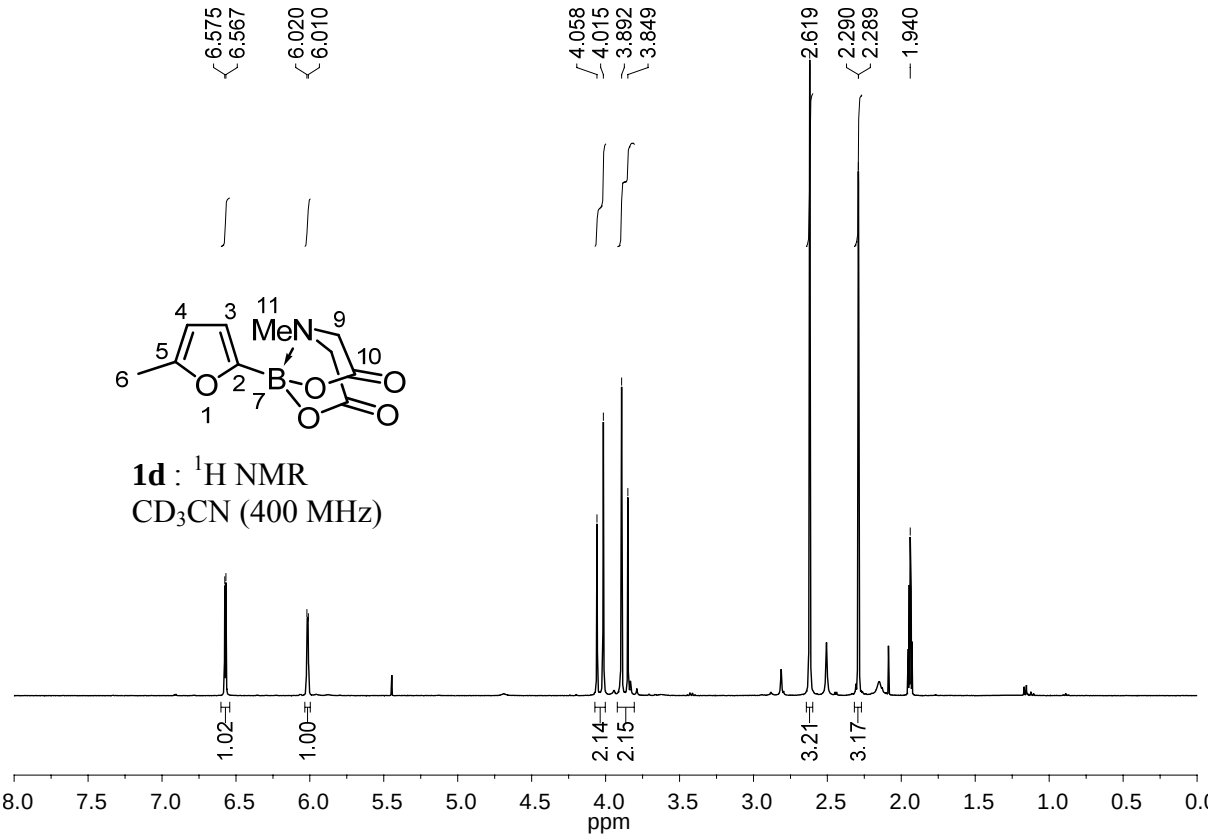
1c : ^{1}H NMR
CD_3CN (400 MHz)



1c : ^{13}C NMR
CD_3CN (100 MHz)



1c : ^{11}B NMR
CD_3CN (128.3 MHz)



1d : ^{1}H NMR
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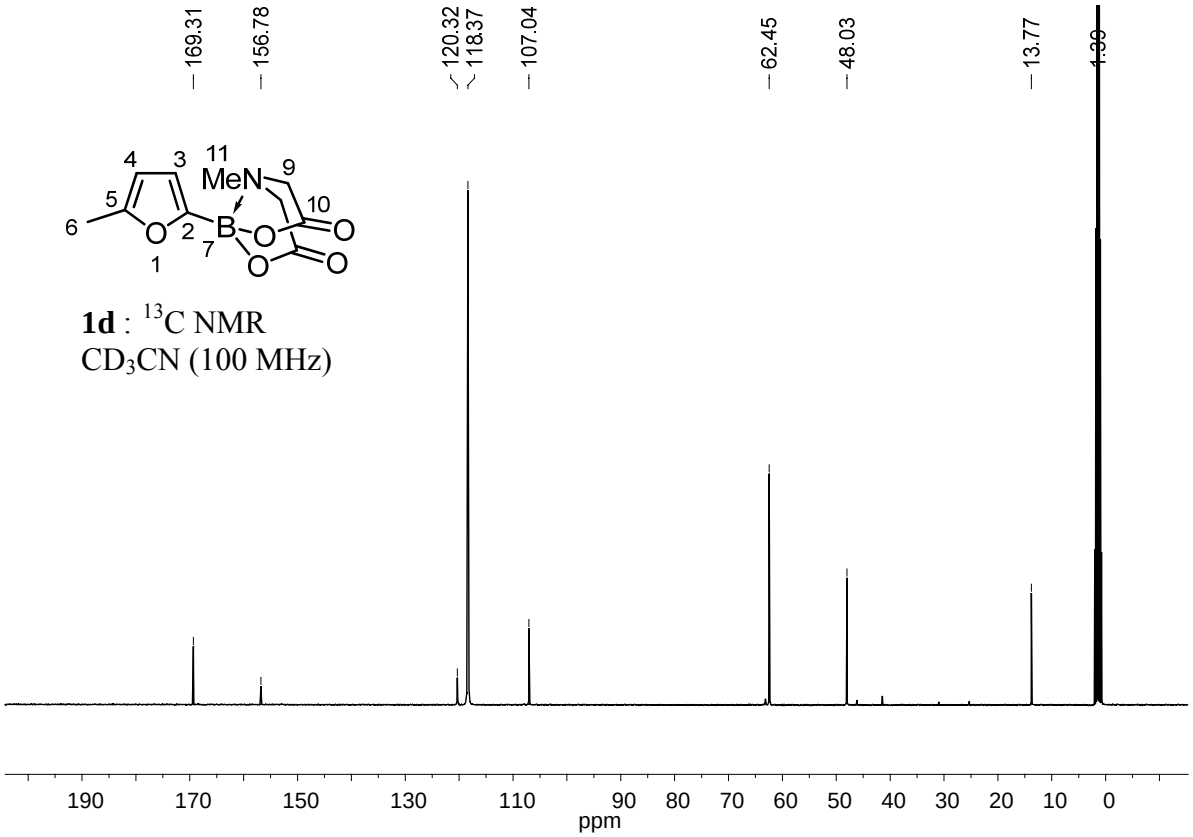
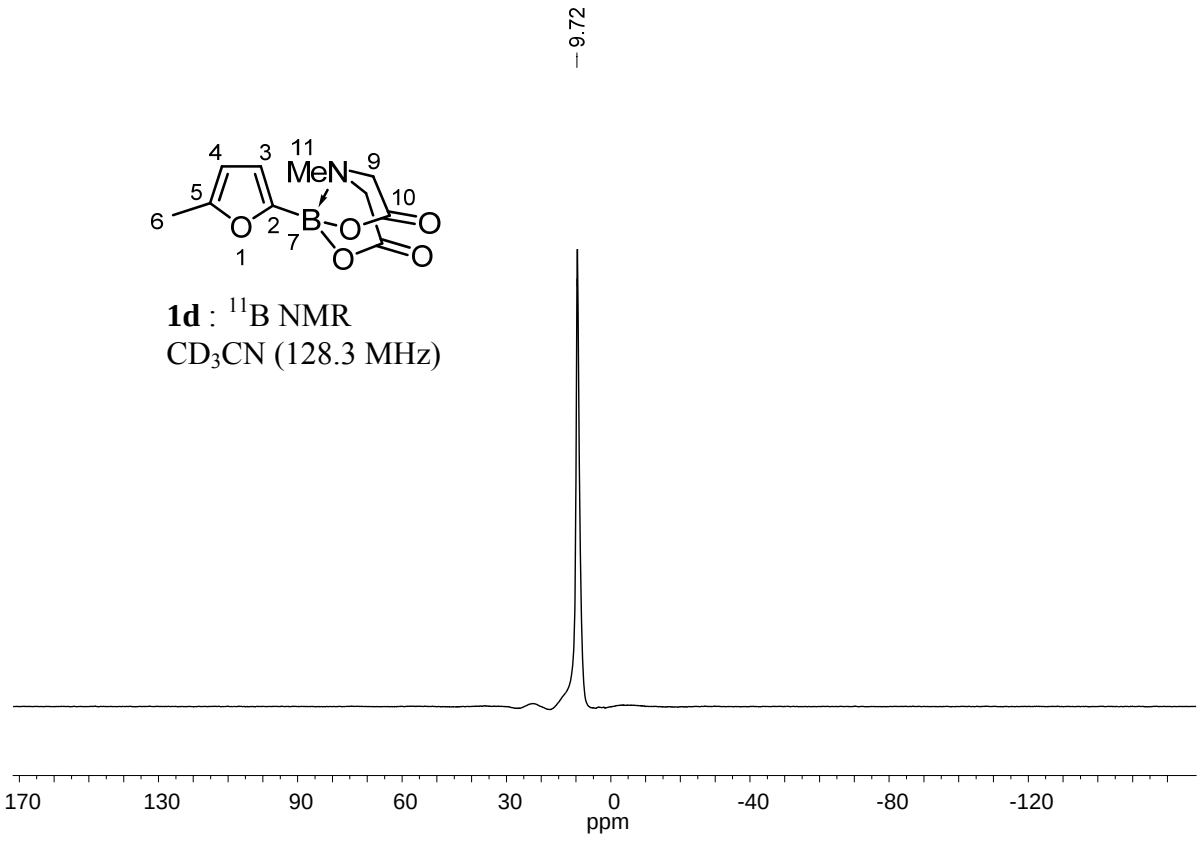
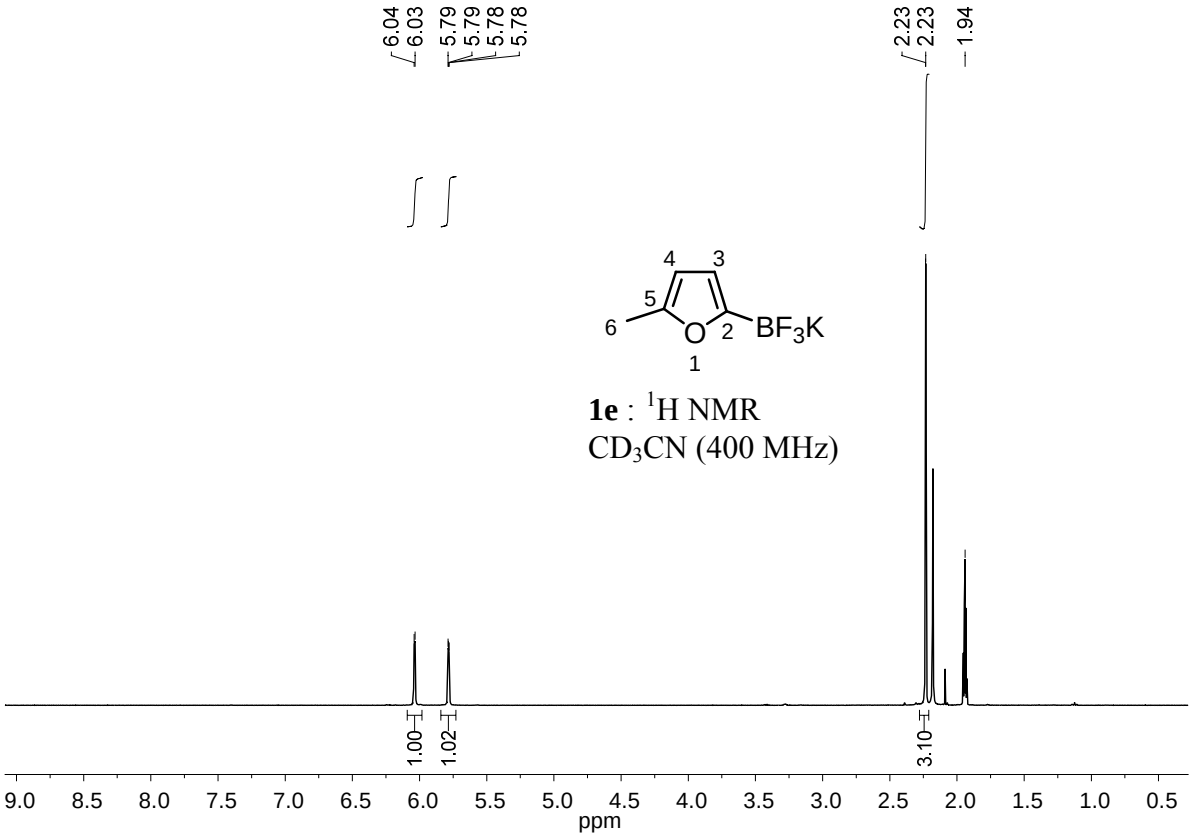


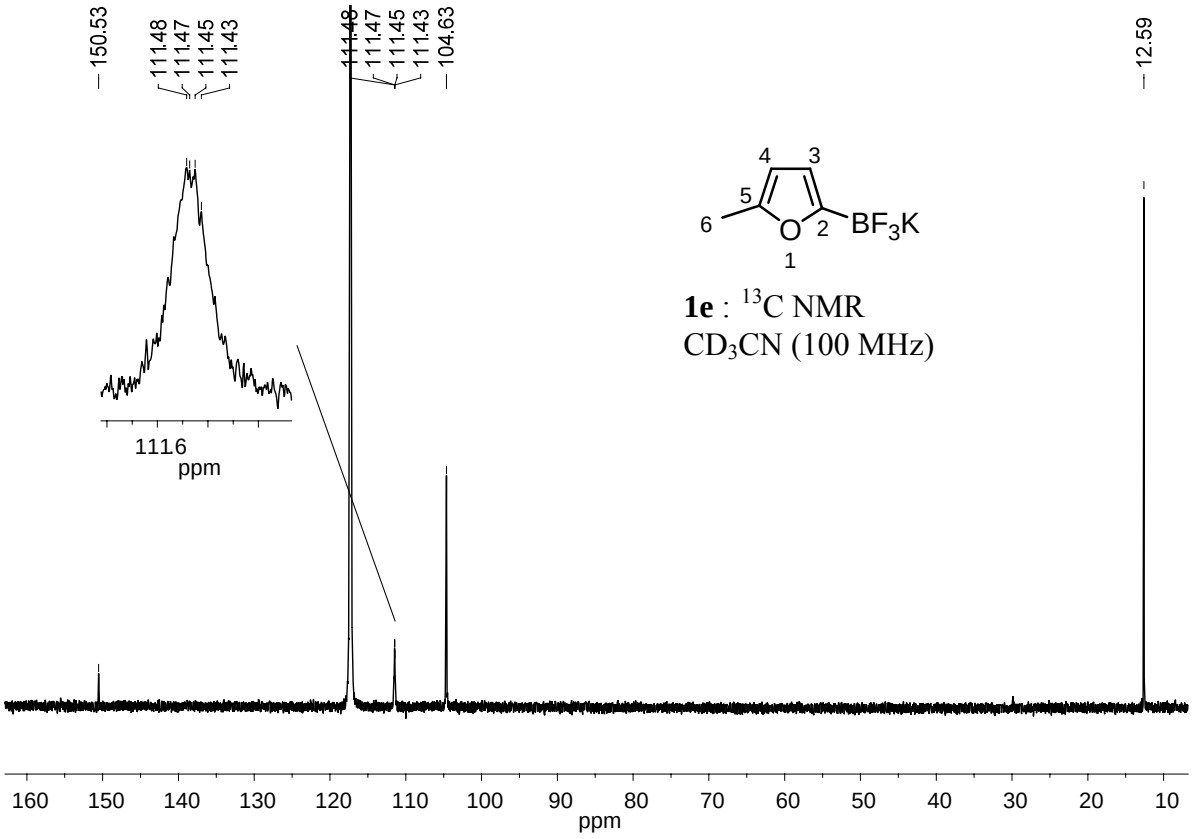
1d : ^{13}C NMR
CD_3CN (100 MHz)



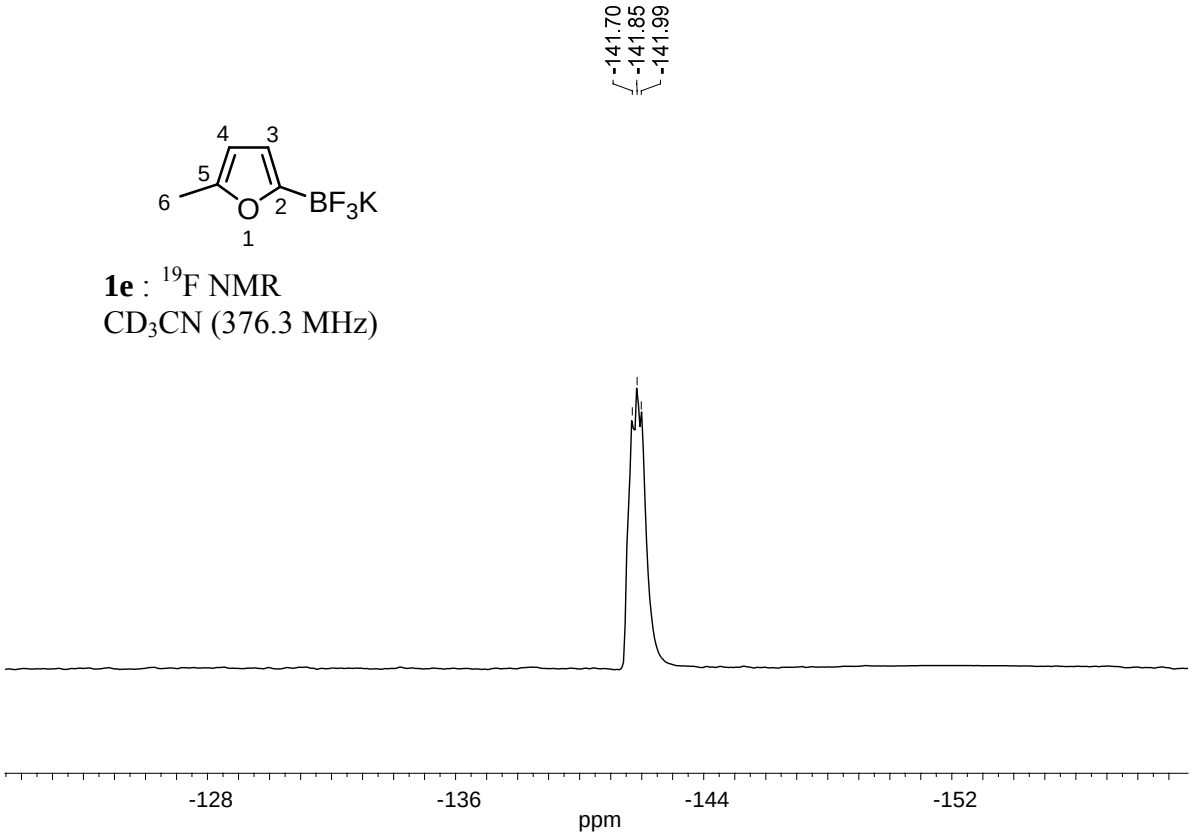
1d : ^{11}B NMR
CD_3CN (128.3 MHz)



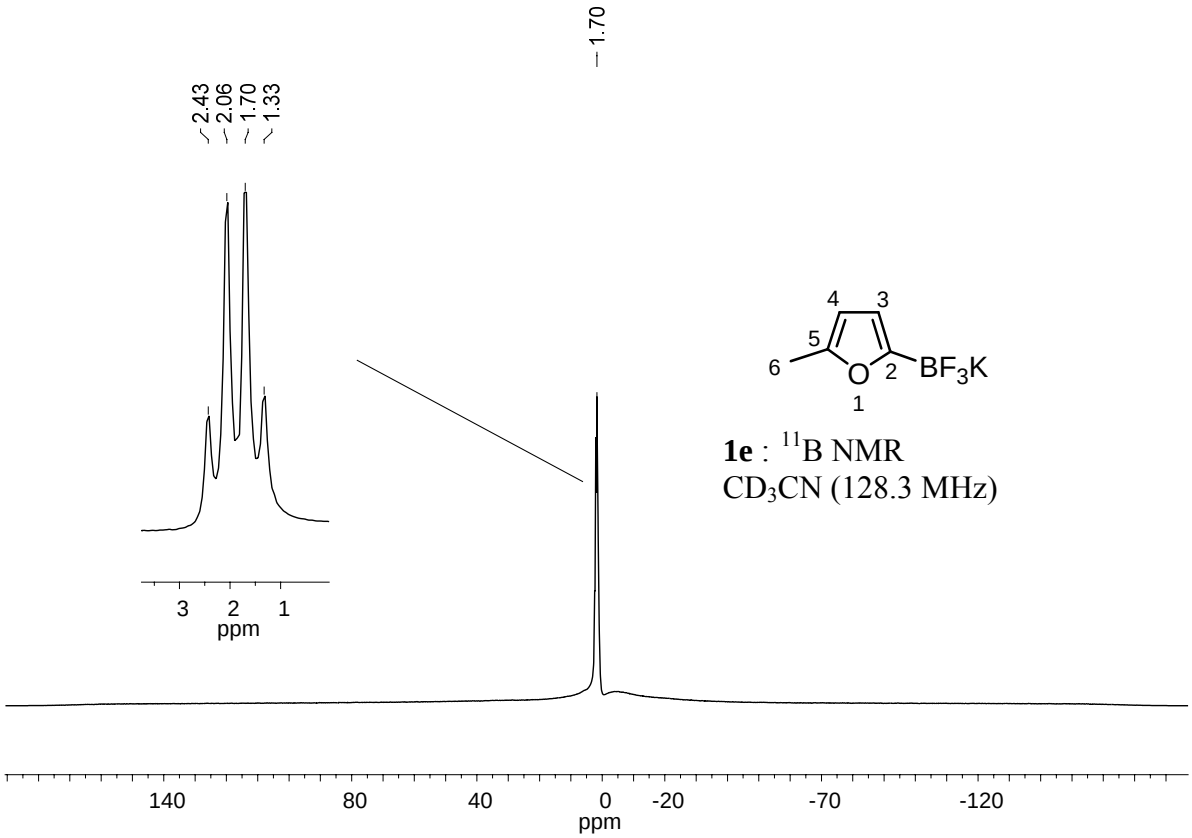
1e : ^{1}H NMR
CD_3CN (400 MHz)



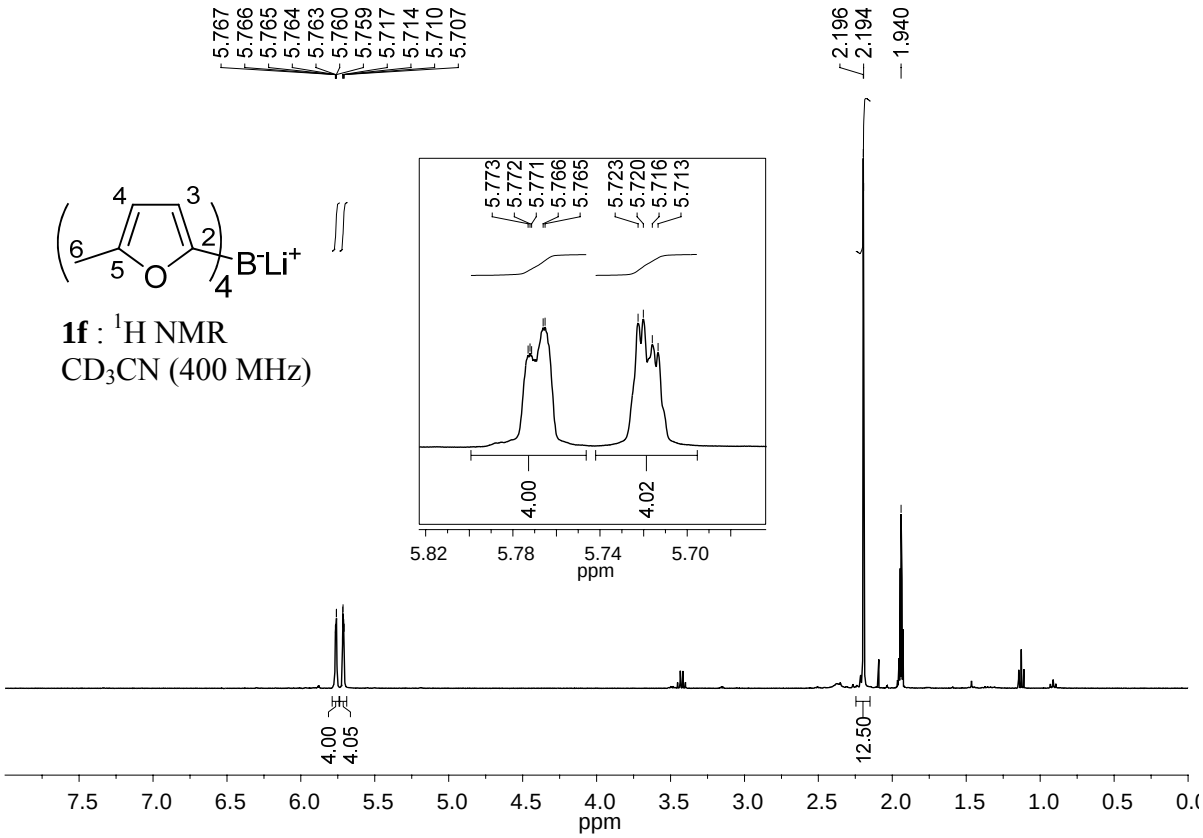
1e : ^{13}C NMR
CD_3CN (100 MHz)



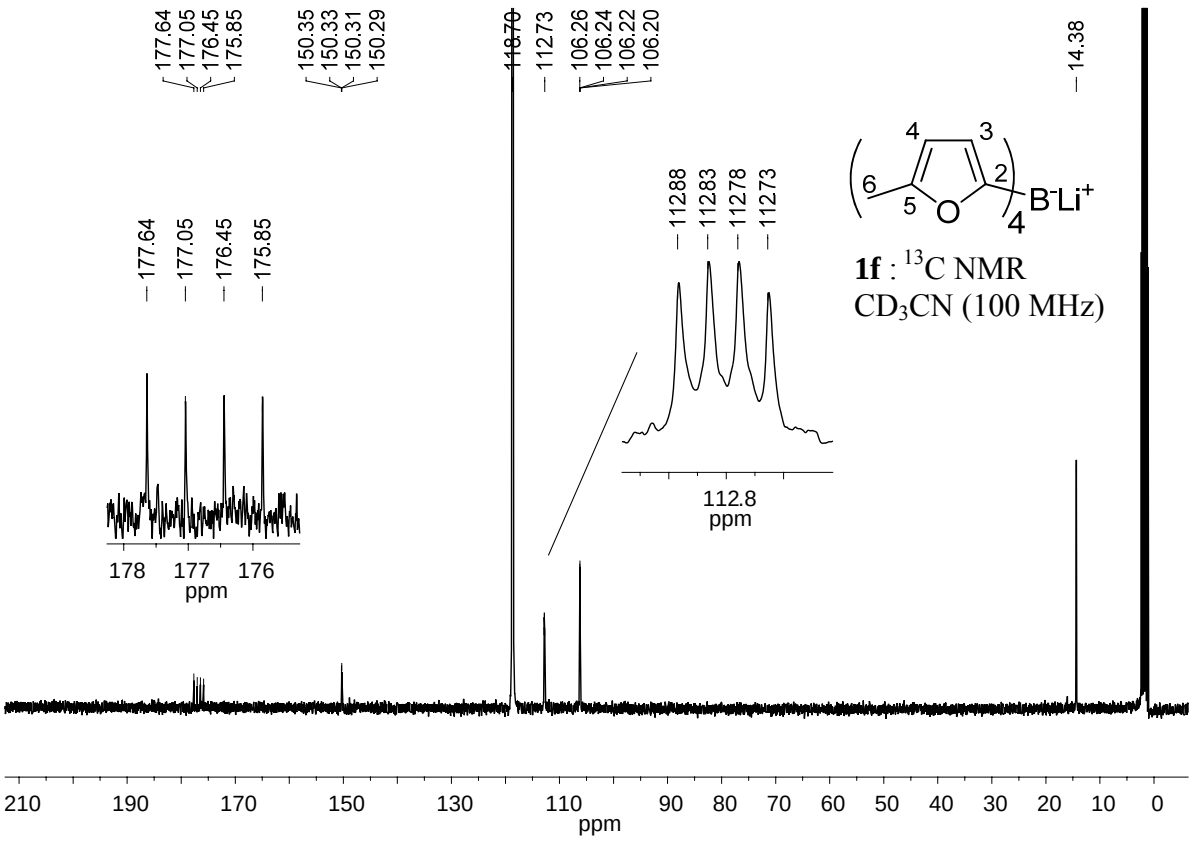
1e : ^{19}F NMR
CD_3CN (376.3 MHz)



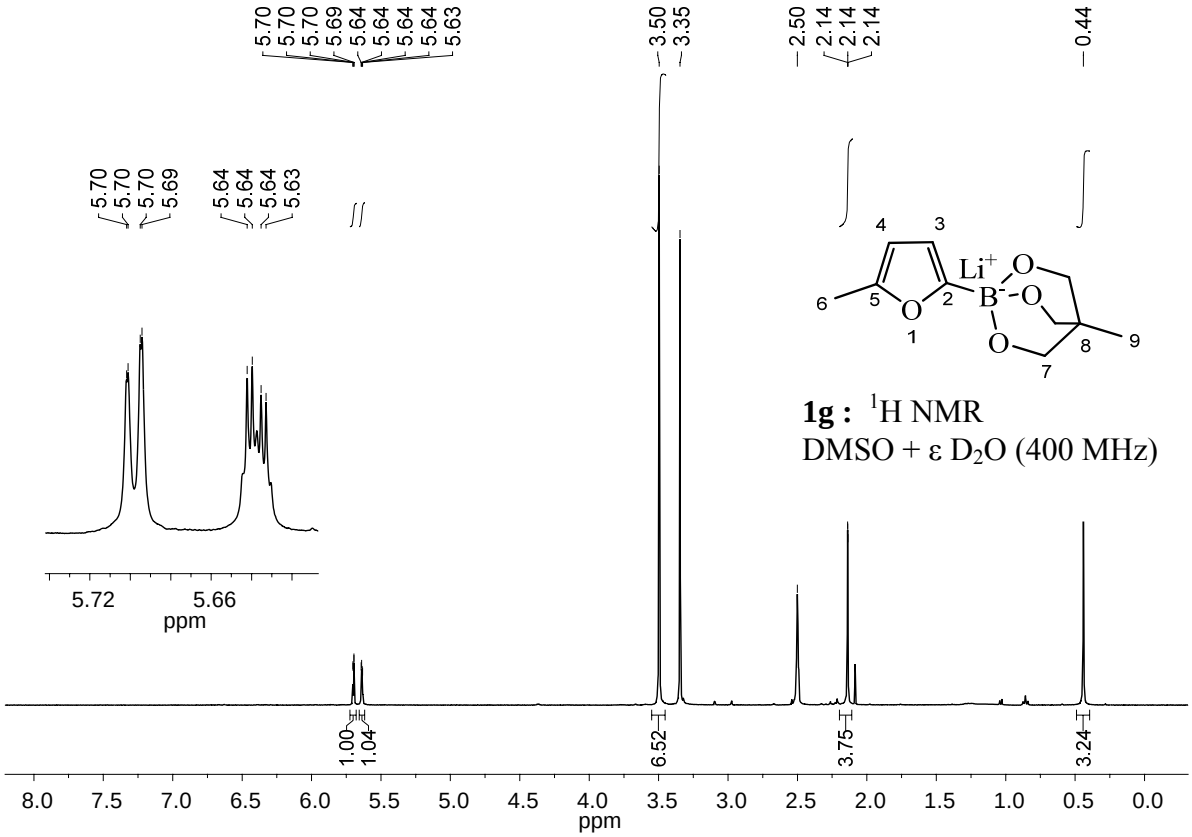
1e : ^{11}B NMR
CD_3CN (128.3 MHz)



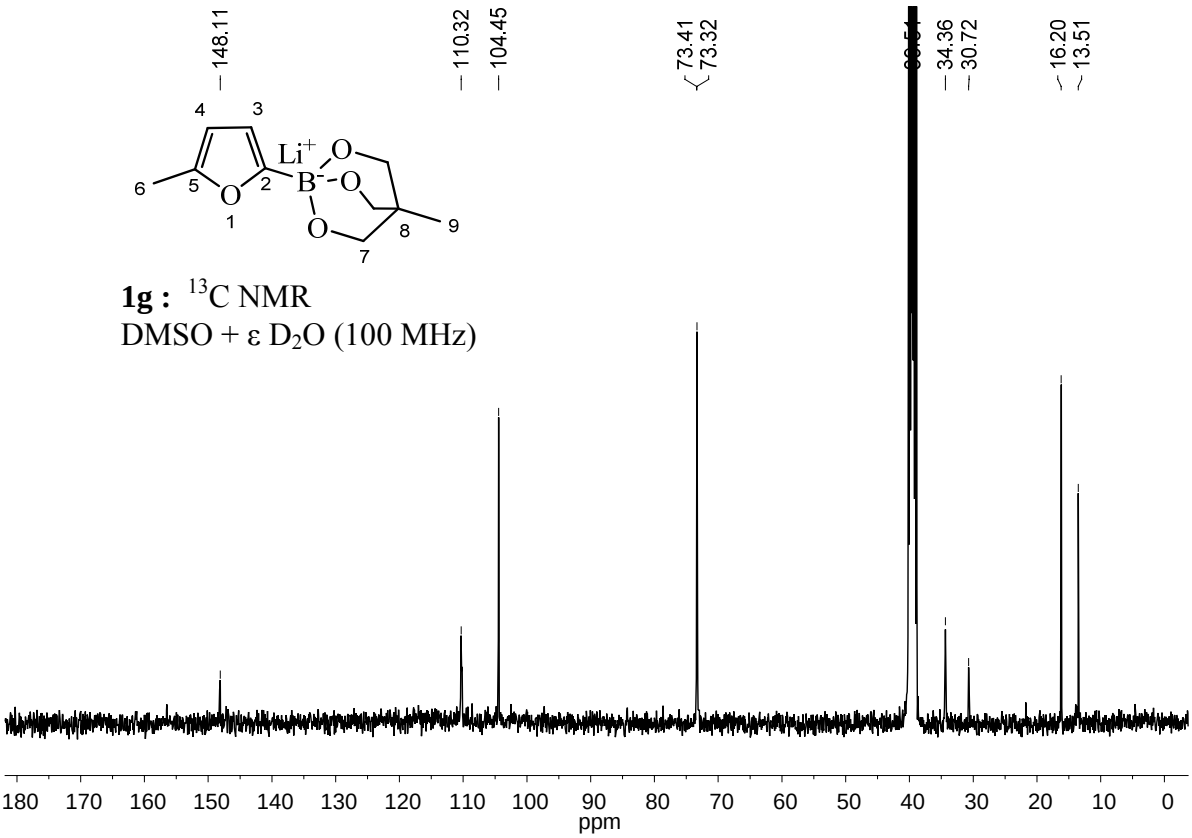
1f : ^{1}H NMR
CD_3CN (400 MHz)



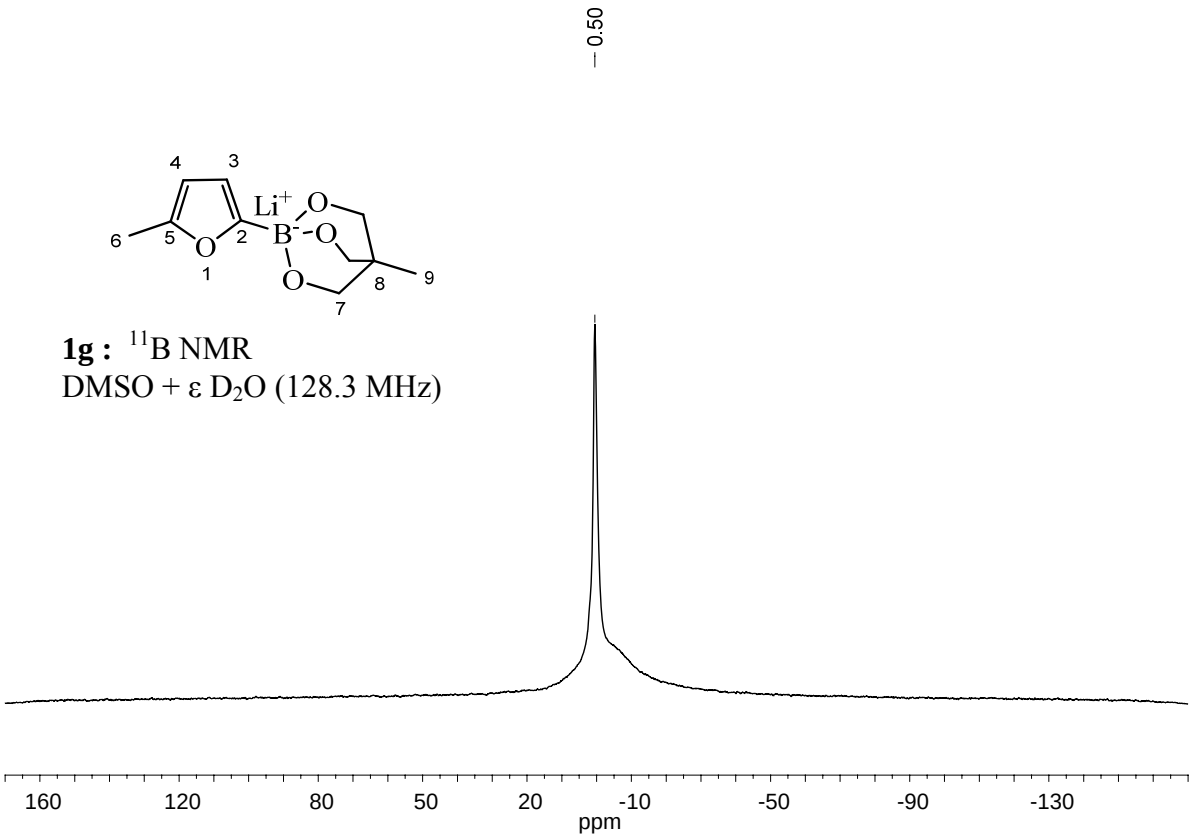
1f : ^{13}C NMR
CD_3CN (100 MHz)



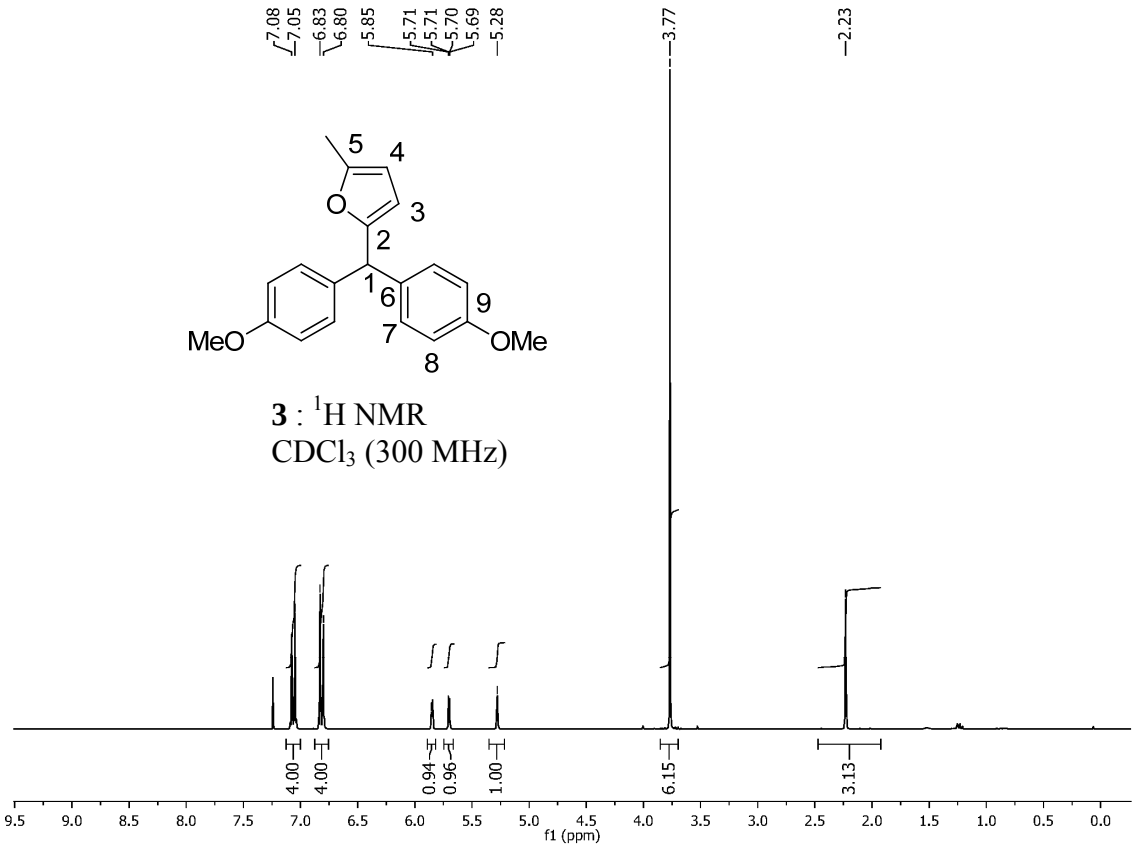
1g : ^{1}H NMR
DMSO + ε D_2O (400 MHz)



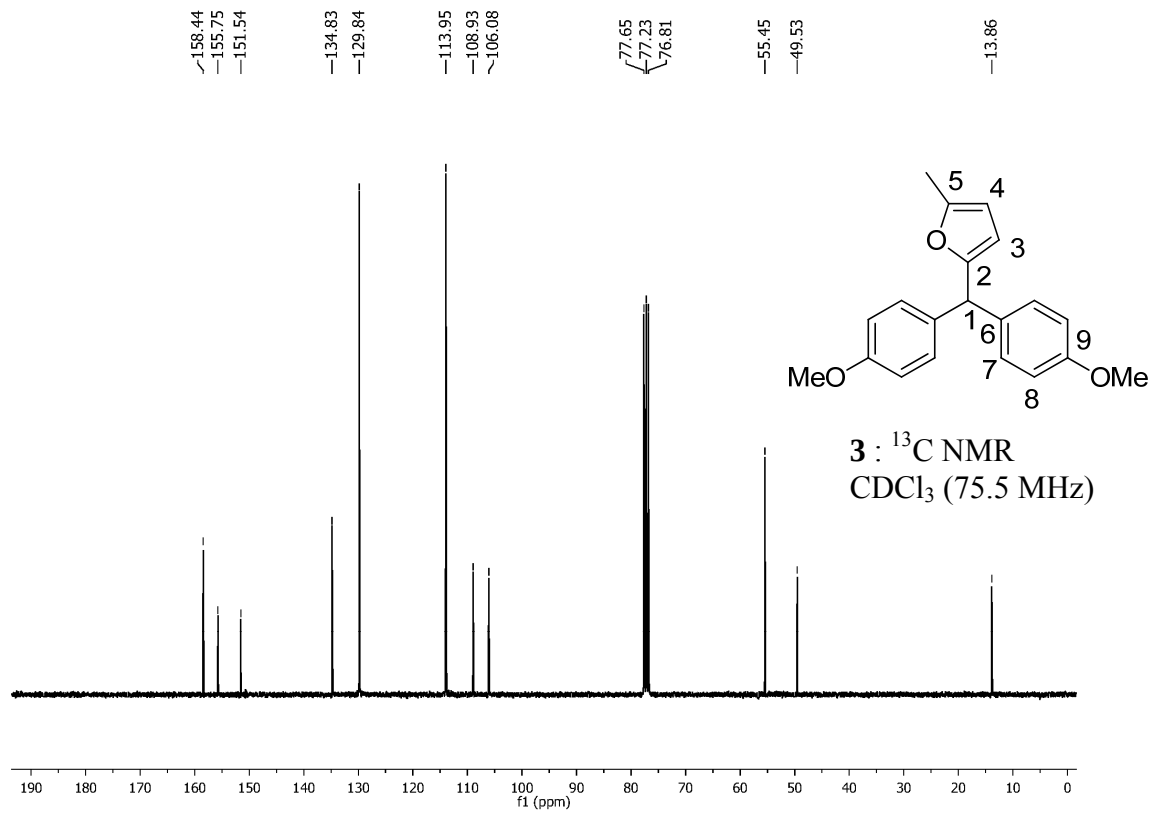
1g : ^{13}C NMR
DMSO + ε D_2O (100 MHz)



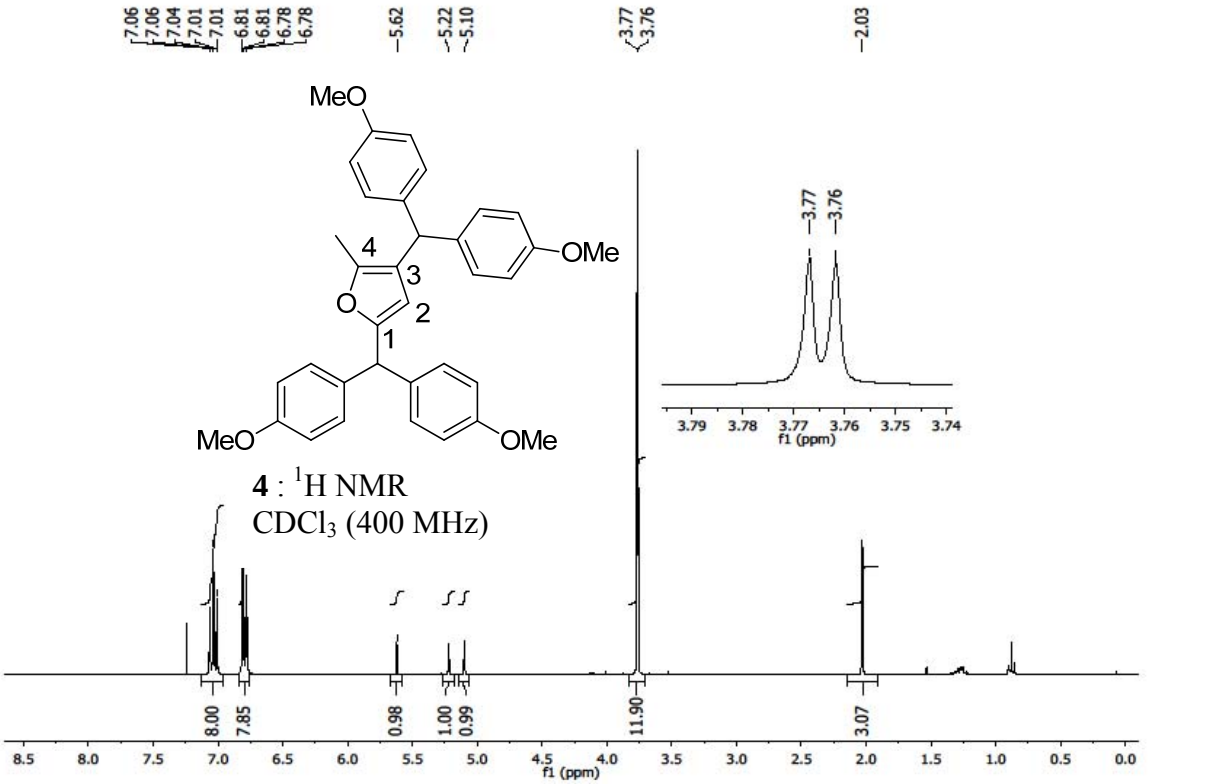
1g : ^{11}B NMR
DMSO + ε D_2O (128.3 MHz)



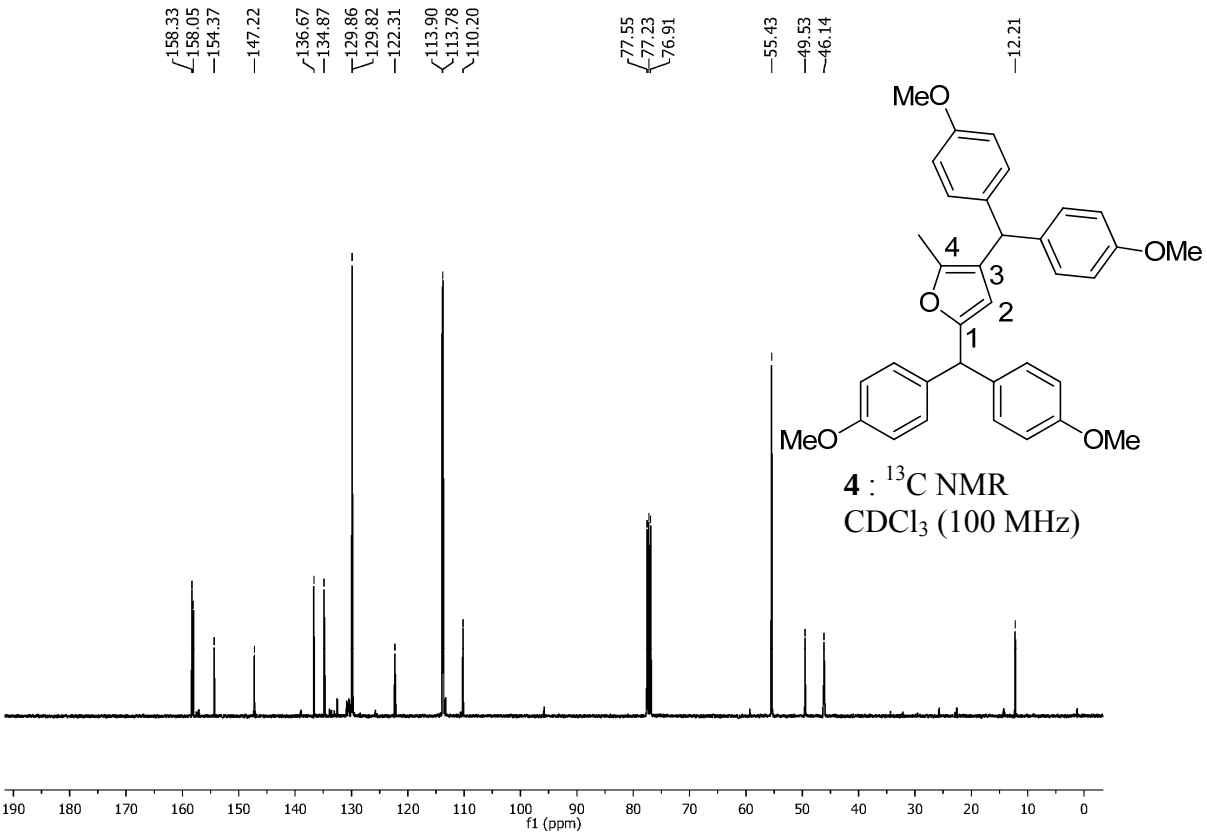
3 : ^{1}H NMR
$CDCl_3$ (300 MHz)



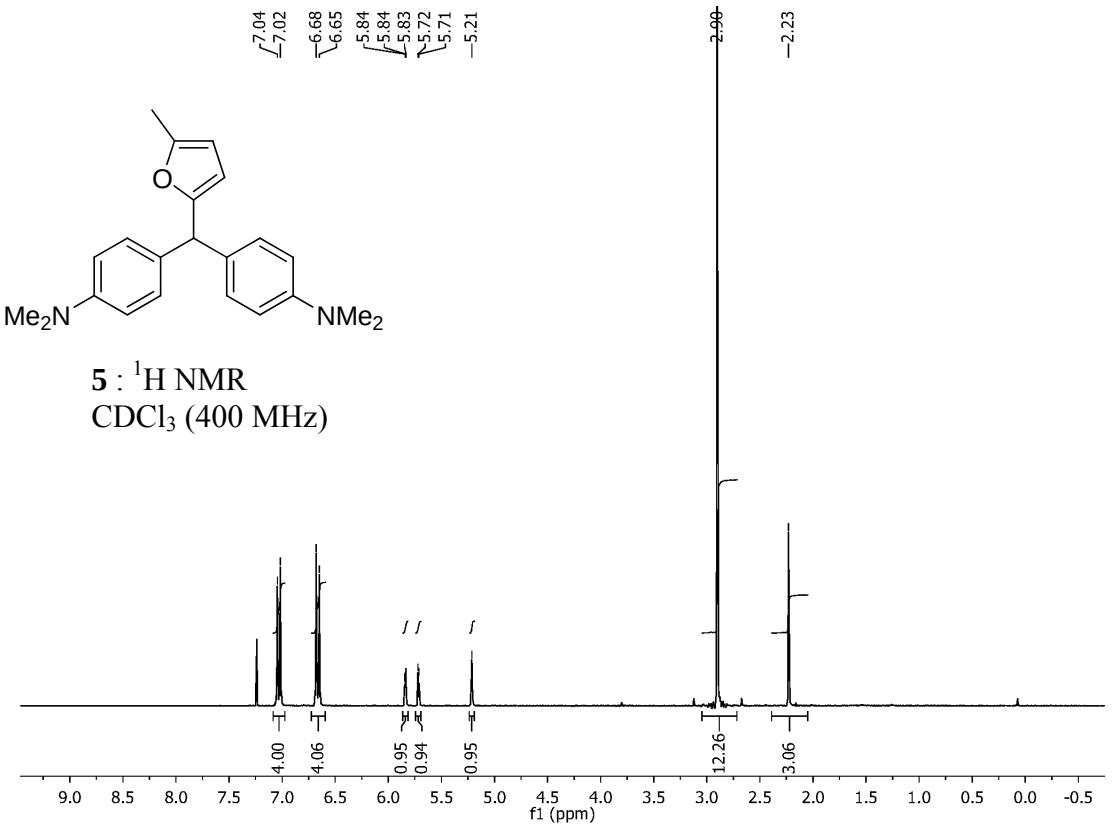
3 : ^{13}C NMR
$CDCl_3$ (75.5 MHz)



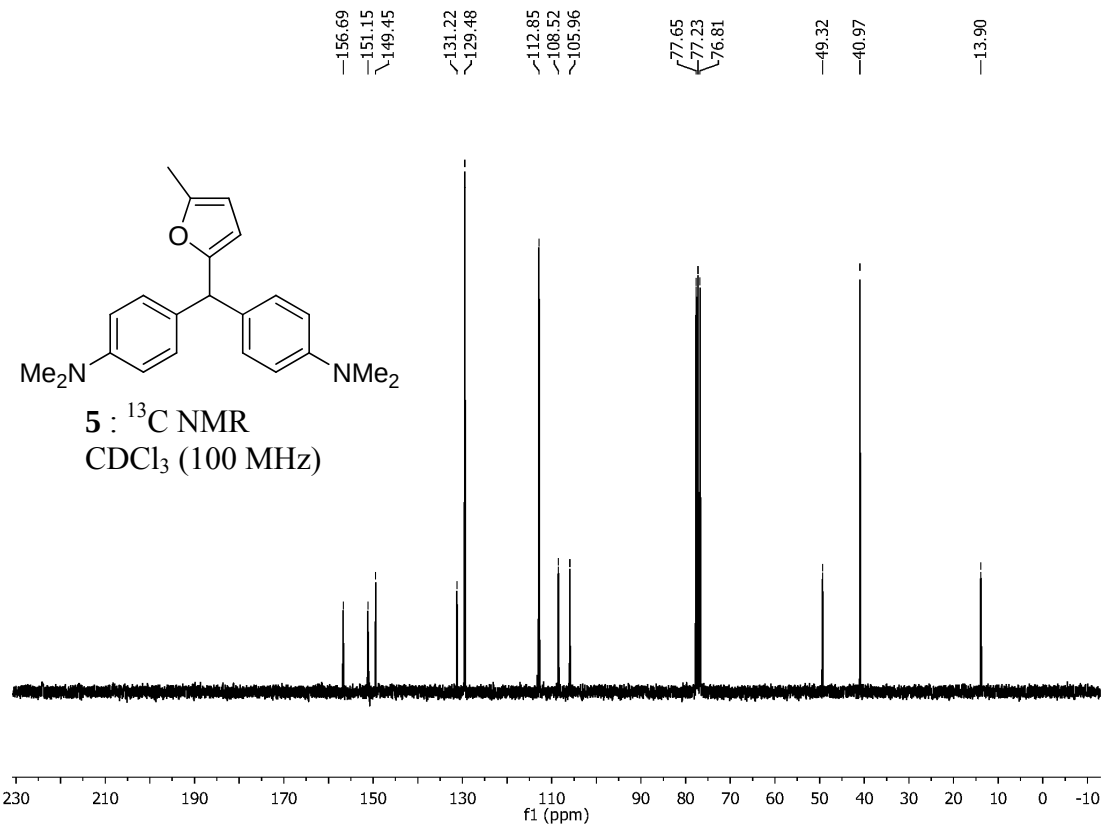
4 : ^{1}H NMR
$CDCl_3$ (400 MHz)



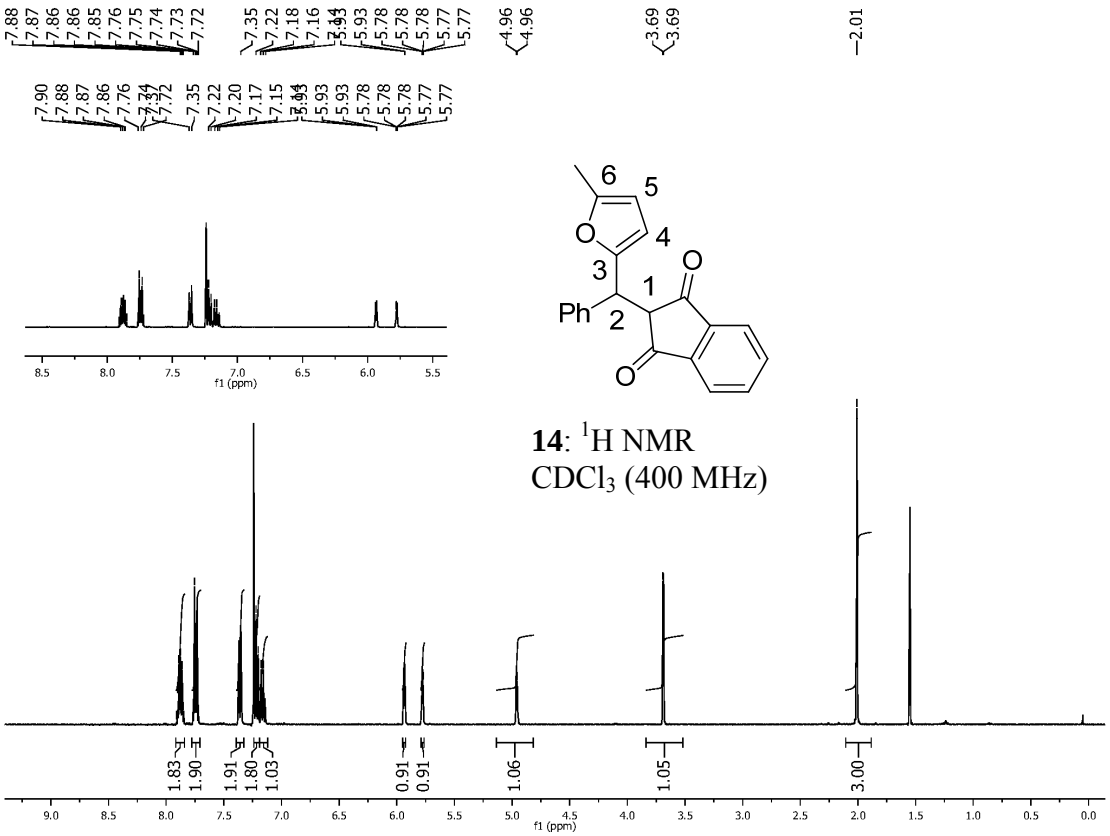
4 : ^{13}C NMR
$CDCl_3$ (100 MHz)



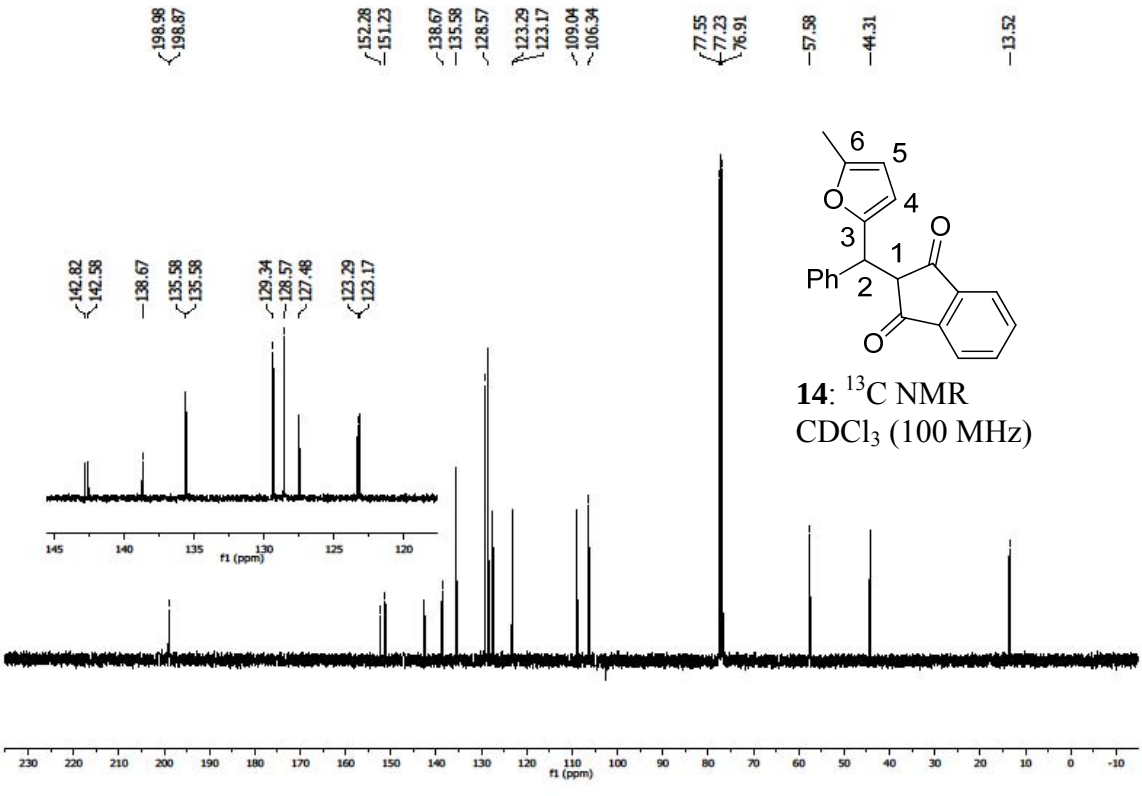
5 : ^{1}H NMR
$CDCl_3$ (400 MHz)



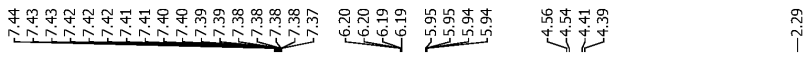
5 : ^{13}C NMR
$CDCl_3$ (100 MHz)

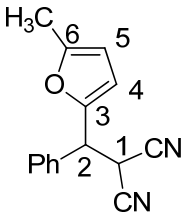


14: ^{1}H NMR
$CDCl_3$ (400 MHz)

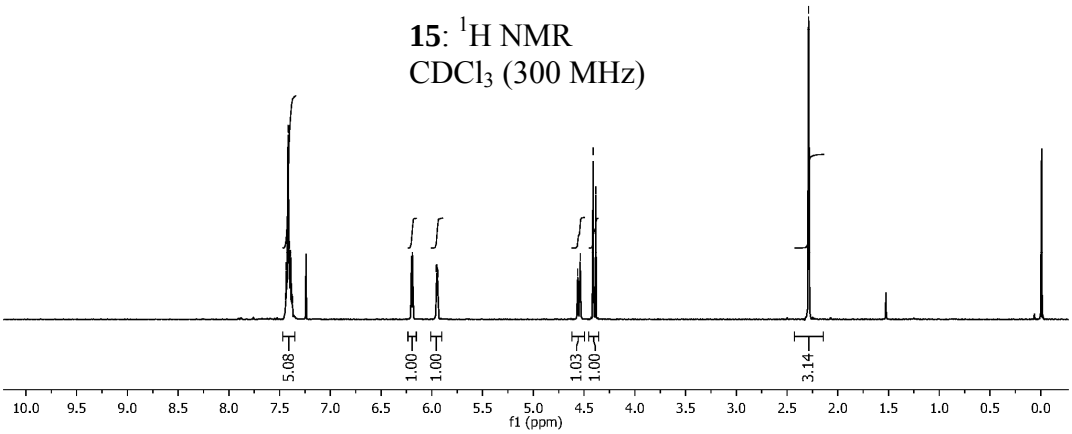


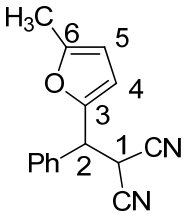
14: ^{13}C NMR
$CDCl_3$ (100 MHz)



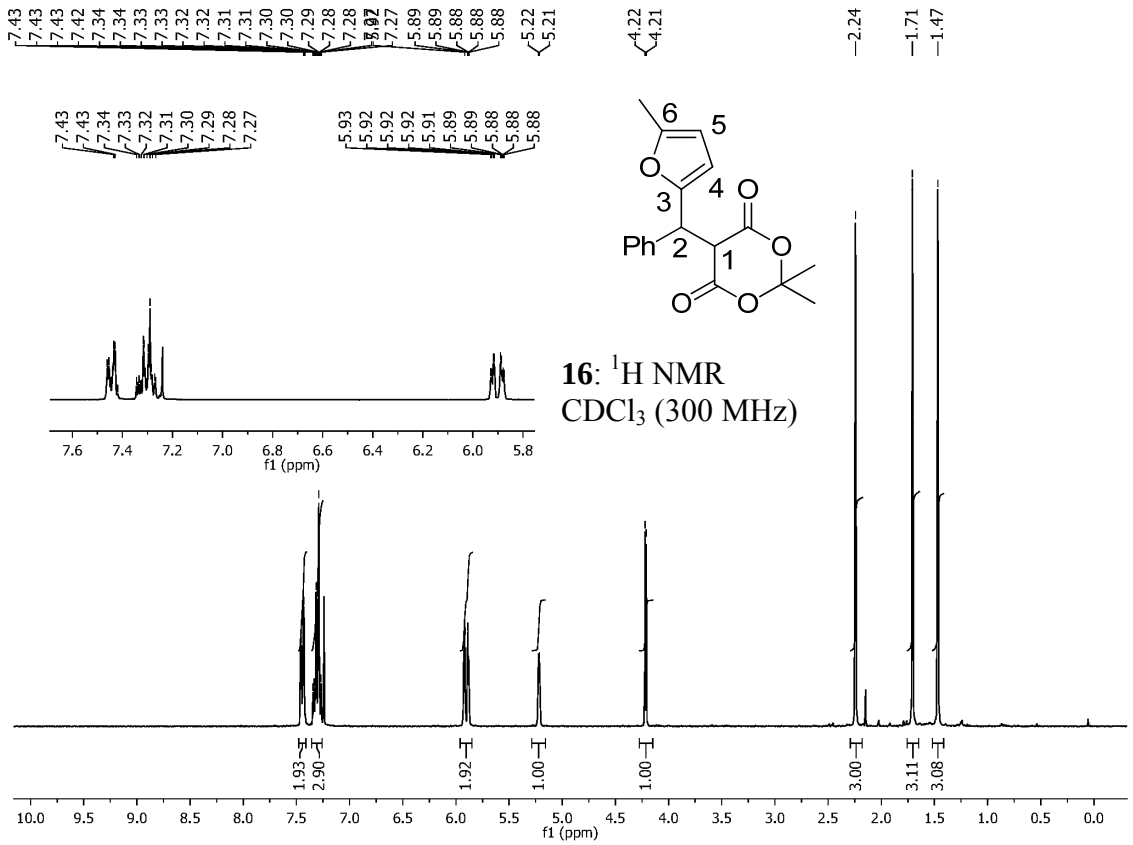


15: ^{1}H NMR
$CDCl_3$ (300 MHz)

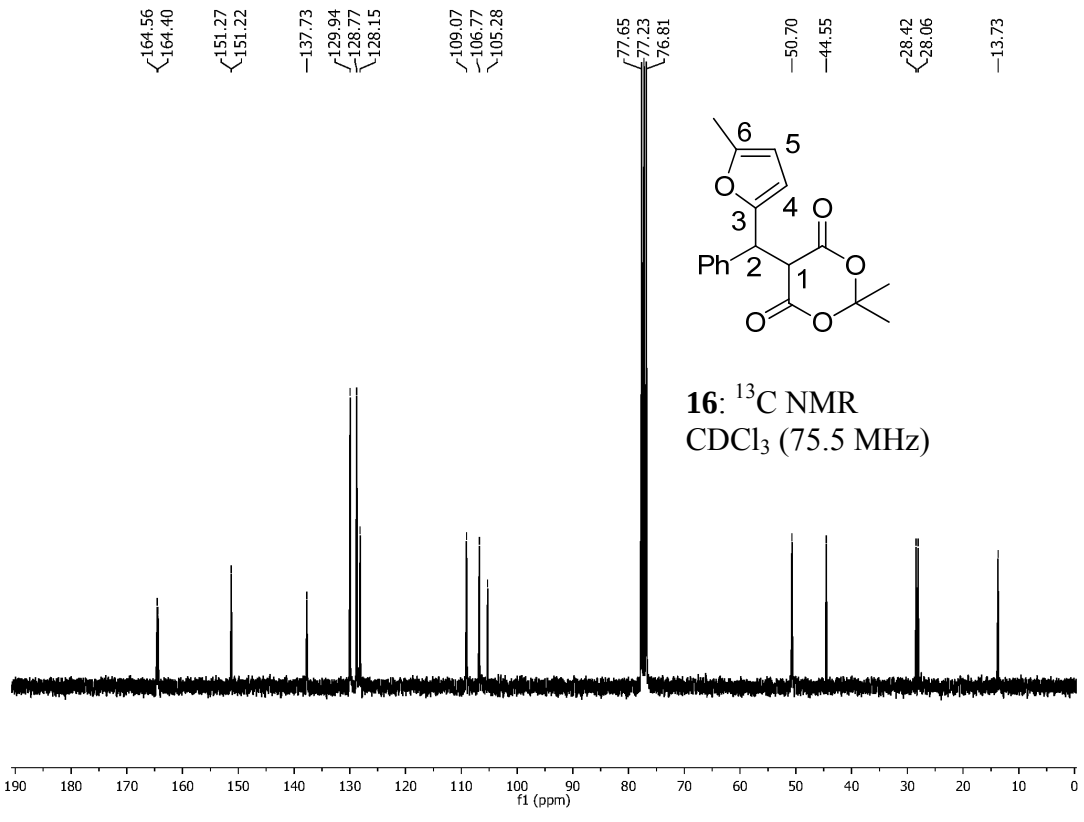




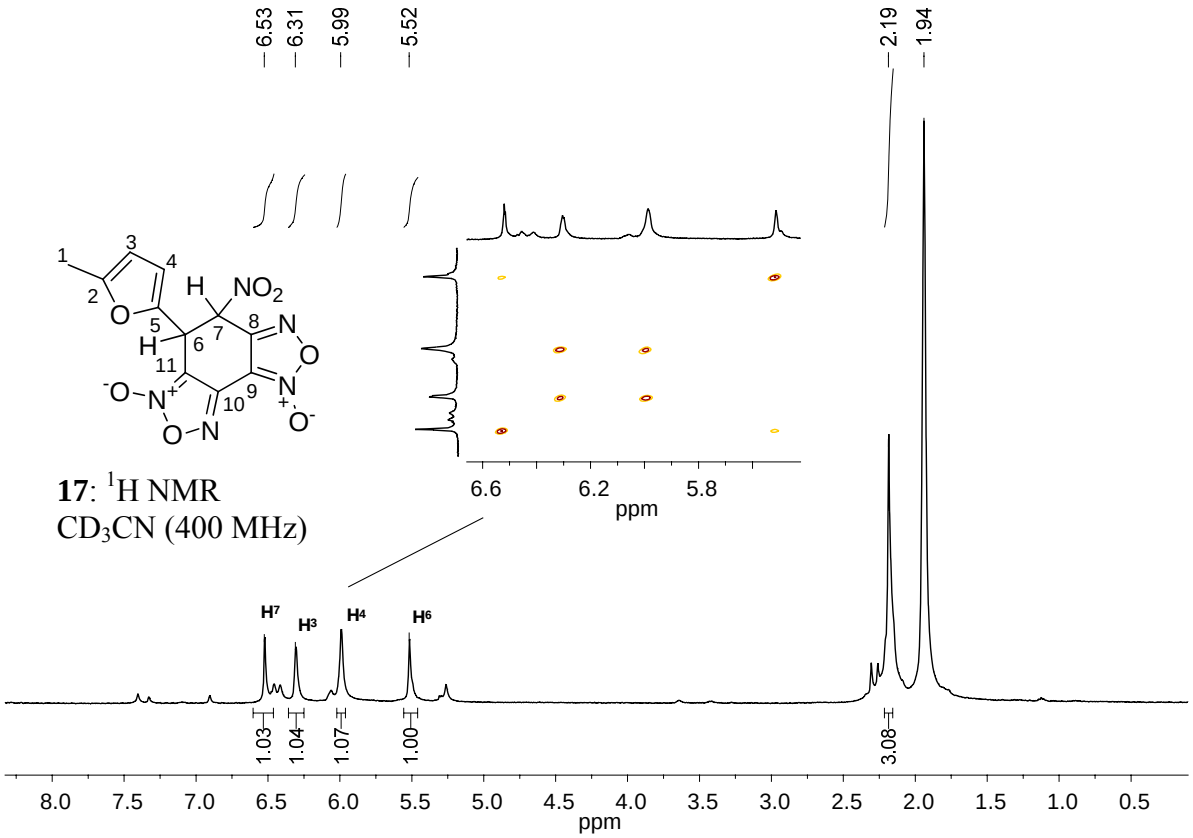
15: ^{13}C NMR
$CDCl_3$ (75.5 MHz)



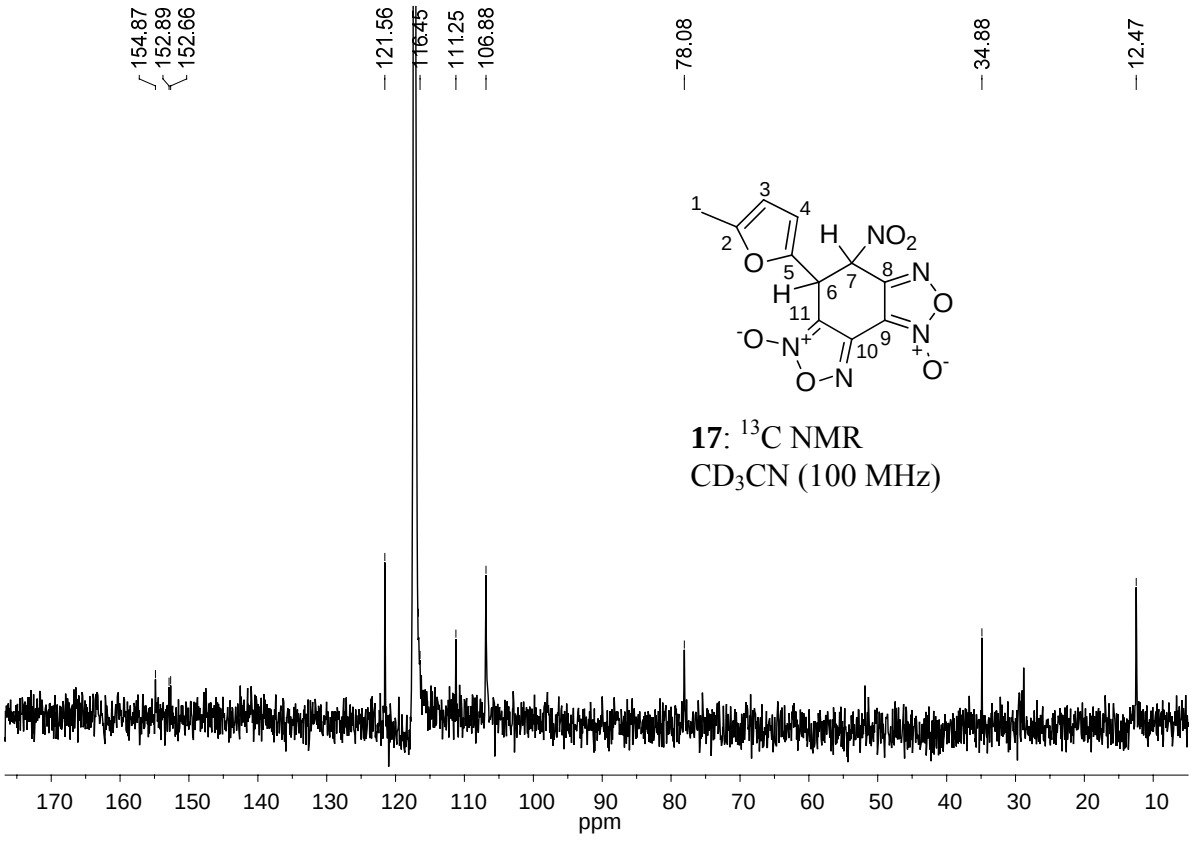
16: ^{1}H NMR
$CDCl_3$ (300 MHz)



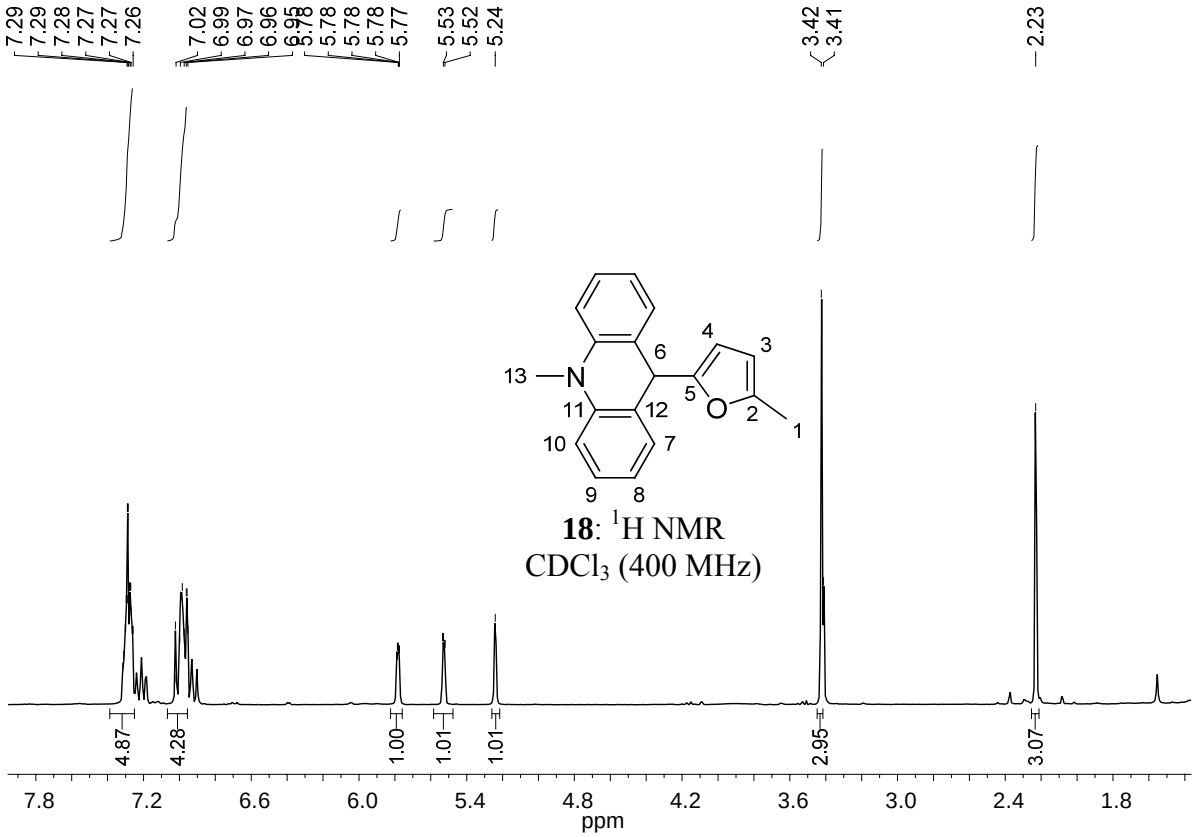
16: ^{13}C NMR
$CDCl_3$ (75.5 MHz)



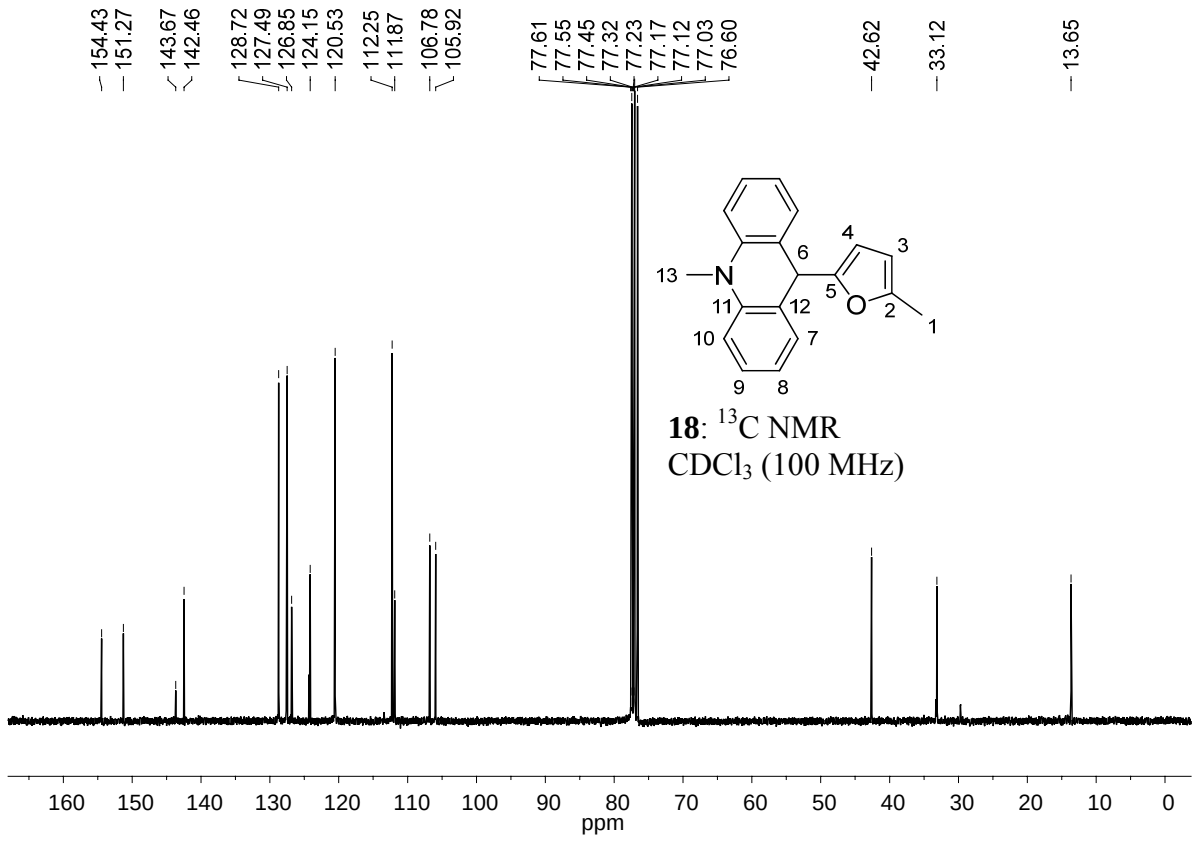
17: ^{1}H NMR
CD_3CN (400 MHz)



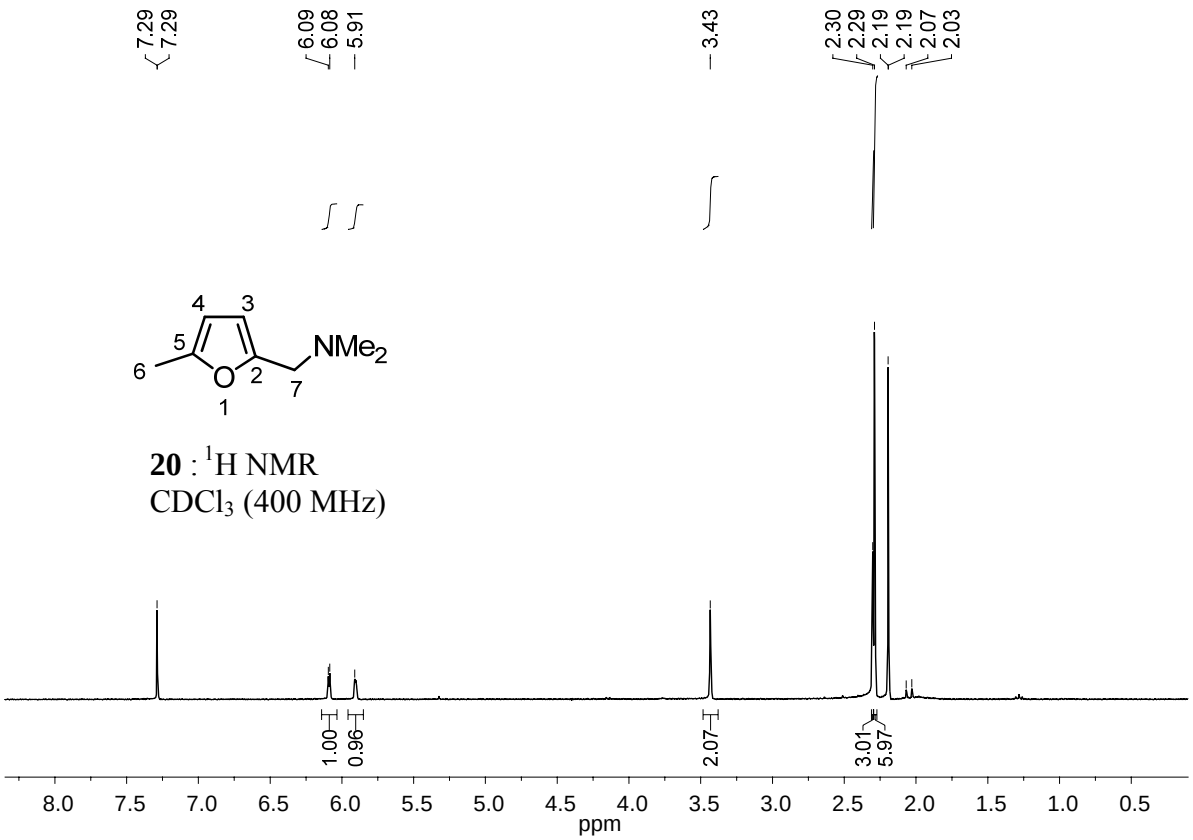
17: ^{13}C NMR
CD_3CN (100 MHz)



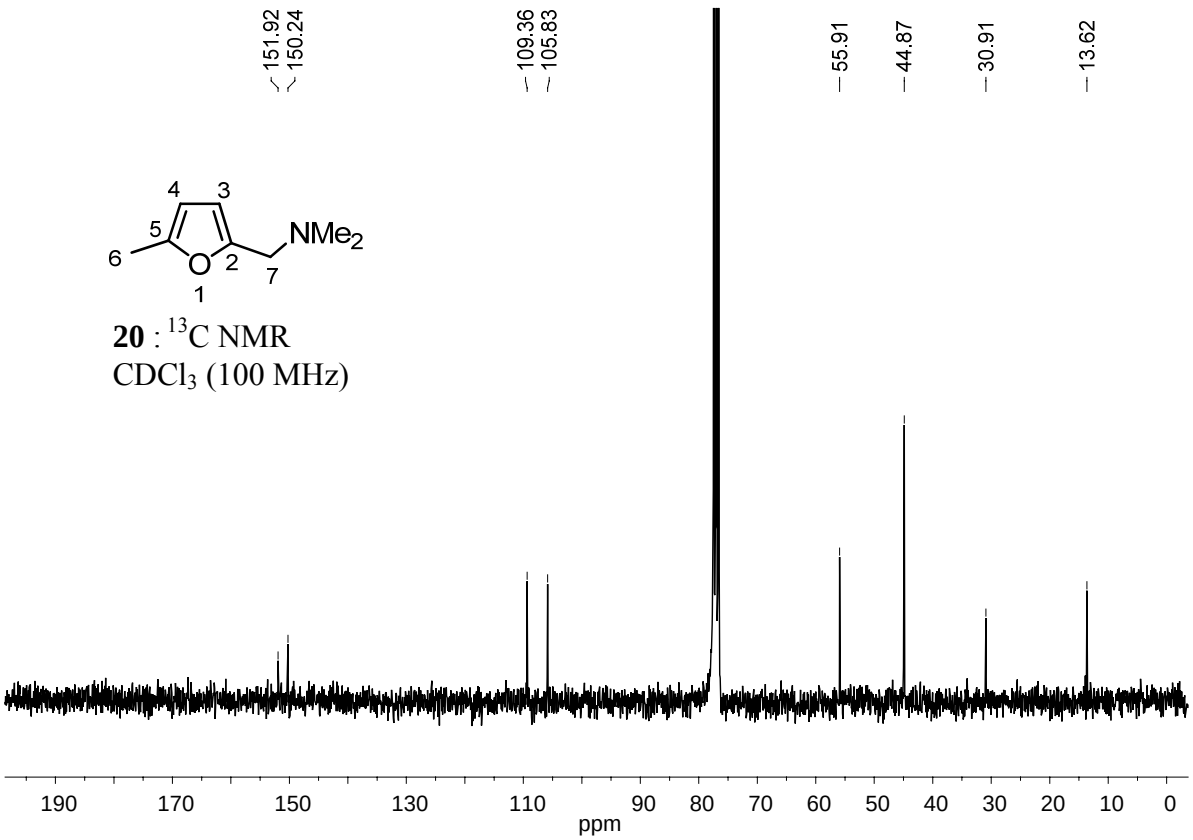
18: ^{1}H NMR
$CDCl_3$ (400 MHz)



18: ^{13}C NMR
$CDCl_3$ (100 MHz)



20 : ^{1}H NMR
$CDCl_3$ (400 MHz)



20 : ^{13}C NMR
$CDCl_3$ (100 MHz)