SUPPORTING INFORMATION

Self-supported polymeric ruthenium complexes as olefin metathesis catalysts in synthesis of heterocyclic compounds

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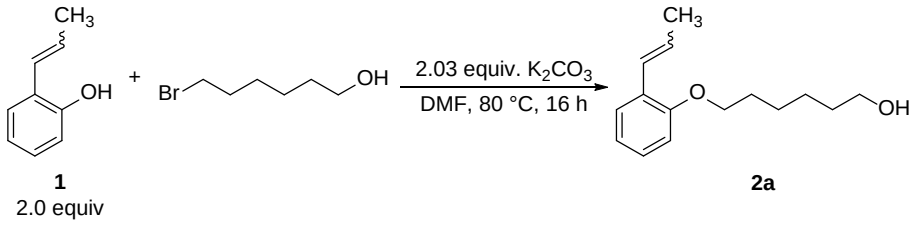
1. General Information

All reactions requiring the exclusion of oxygen and moisture were performed in dry glassware with dry solvents (SPS MBraun), under a dry and oxygen-free argon atmosphere using standard Schlenk technique. The addition of dry solvents or reagents was carried out using argon flushed stainless steel cannulas and plastic syringes. Analytical thin layer chromatography (TLC) was performed on Merck Silica gel 60 F254 precoated aluminum sheets. Components were visualized by observation under UV light (254 or 365 nm) or dyed by aqueous $KMnO_4$ reagent. Flash column chromatography was carried out using silica gel 60 (230 – 400 mesh), purchased from Merck. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopic data were collected on Varian 400 MHz spectrometer at ambient temperature. The chemical shifts are reported in ppm relative to solvent peaks. GC chromatograms were recorded using PerkinElmer Clarus 580 with IntertCap 5MS-Sil column. GC conversions were determined based on the ratio of an internal standard (1,2,4,5-tetramethylbenzene) and the starting material. High resolution mass spectra were recorded on Thermo QExactive and AutoSpec Premier mass spectrometer. MALDI-TOF analysis were recorded on Waters SYNAPT G2-Si (qToF type) spectrometer. IR spectra were recorded on JASCO FT/IR-6200 spectrometer with ATR attachment. Elemental analyses were carried out at the Polish Academy of Sciences, Institute of Organic Chemistry.

Ru-4 was synthesized in accordance to literature.[1] RCM substrates was synthesized according to literature: **7a**[2], **7b**[3], **7c**[4], **7d**[5], **7e**[6], **7f**[7], **7g**[8]. Unless otherwise noted, all materials were purchased from commercial suppliers and used as received.

2. Preparation of NHC precursors and complexes

2.1. 6-[2-(Prop-1-en-1-yl)phenoxy]hexan-1-ol (2a)



1
2.0 equiv

2a

250 mL round-bottomed flask was evacuated and refilled with argon (3 times), then under the argon atmosphere, 2-(prop-1-en-1-yl)phenol (**1**) (6.56 mL, 50.0 mmol) and 6-bromo-1-hexanol (3.37 mL, 25.0 mmol) were dissolved in anhydrous DMF (70 mL), followed by addition of K_2CO_3 (7.09 g, 50.7 mmol). The resulting mixture was stirred at 80 °C for 16 h, under argon atmosphere. After cooling to room temperature AcOEt (140 mL) was added and the resulting mixture was washed with water (3 x 100 mL) and brine (100 mL), then organic phase was dried over anh. Na_2SO_4, filtered, and volatiles were evaporated *in vacuo*. The resulting crude product was purified by column chromatography (*n*-hex/AcOEt 9:1 to 3:1), providing product as a yellowish, dense liquid (4.35 g, **74%** yield, *E*/*Z* = 56:44).

Major isomer (*E*):

R_f = 0.13 (*n*-hex/AcOEt 4:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, J = 7.6, 1.7 Hz, 1H), 7.15 (ddd, J = 8.2, 7.5, 1.7 Hz, 1H), 6.92 (tdd, J = 7.1, 1.5, 0.8 Hz, 1H), 6.83 (dd, J = 8.2, 1.0 Hz, 1H), 6.72 (dq, J = 15.9, 1.7 Hz, 1H), 6.24 (dq, J = 15.9, 6.6 Hz, 1H), 3.98 (t, J = 6.5 Hz, 2H), 3.67 (dd, J = 10.8, 5.4 Hz, 2H), 1.90 (dd, J = 6.6, 1.8 Hz, 3H), 1.83 – 1.78 (m, 1H), 1.61 (td, J = 13.0, 6.4 Hz, 2H), 1.56 – 1.40 (m, 6H).

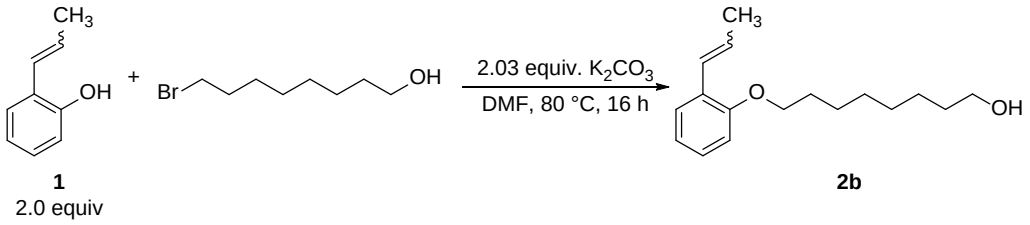
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 130.2, 127.8, 127.2, 126.5, 125.8, 120.6, 112.0, 68.3, 63.0, 32.8, 29.4, 26.1, 25.7, 19.1.

HRMS (ESI): *m/z* 257.1514 ($[M+Na]^+$, $C_{15}H_{22}O_2Na^+$ calcd. 257.1517).

EA: Anal. calcd. for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.63; H, 9.60.

FT-IR-ATR: 3334, 3030, 2933, 2859, 1596, 1448, 1239, 1110, 1048, 746 cm^{-1}.

2.2. 8-[2-(Prop-1-en-1-yl)phenoxy]octan-1-ol (2b)



250 mL round-bottomed flask was evacuated and refilled with argon (3 times), then under the argon atmosphere, 2-(prop-1-en-1-yl)phenol (**1**) (9.58 mL, 73.0 mmol) and 8-bromo-1-heptanol (6.52 mL, 36.5 mmol) were dissolved in anhydrous DMF (100 mL), followed by addition of K_2CO_3 (10.4 g, 74.1 mmol). The resulting mixture was stirred at 80 °C for 16 h, under argon atmosphere. After cooling to the room temperature AcOEt (250 mL) was added, and the resulting mixture was washed with water (3 x 250 mL) and brine (100 mL), then organic phase was dried over anh. Na_2SO_4, filtered, and volatiles were evaporated *in vacuo*. The resulting crude product was purified by column chromatography (*n*-hex/AcOEt 9:1 to 3:1), and then distilled under reduced pressure using Kugelrohr apparatus (p = 0.08 mbar, T = 200 °C) providing product as a colorless, dense liquid (3.20 g, **33%** yield, *E*/*Z* = 4:1). The product contained small amounts of impurities which were unable to remove thus elemental analysis was not performed, however the purity was fair enough to perform next step.

Major isomer (*E*):

R_f = 0.17 (n-hex/AcOEt 4:1)

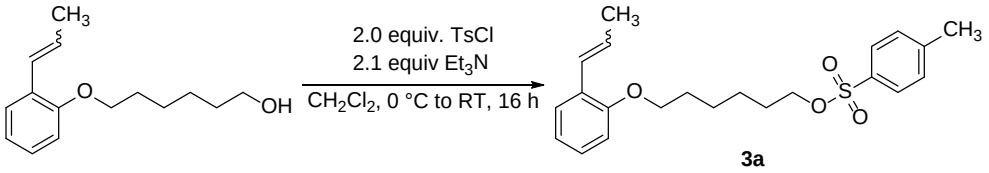
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 7.6, 1.7 Hz, 1H), 7.15 (ddd, J = 8.2, 7.5, 1.7 Hz, 1H), 6.91 – 6.86 (m, 1H), 6.83 (dd, J = 8.2, 1.0 Hz, 1H), 6.72 (dq, J = 15.9, 1.7 Hz, 1H), 6.24 (dq, J = 15.9, 6.6 Hz, 1H), 3.97 (t, J = 6.5 Hz, 2H), 3.65 (t, J = 6.6 Hz, 2H), 1.92 – 1.88 (m, 3H), 1.82 – 1.69 (m, 2H), 1.62 – 1.53 (m, 2H), 1.53 – 1.43 (m, 2H), 1.42 – 1.28 (m, 7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 127.6, 127.1, 126.3, 126.2, 125.7, 120.5, 111.9, 68.3, 63.0, 32.8, 29.34, 29.32, 29.26, 26.1, 25.7, 19.0.

HRMS (ESI): *m/z* 285.1832 ($[M+Na]^+$, $C_{17}H_{26}O_2Na^+$ calcd. 285.1830).

FT-IR-ATR: 3345, 3033, 2927, 2854, 1597, 1385, 1236, 1114, 963, 800, 747 cm^{-1}.

2.3. 6-[2-(Prop-1-en-1-yl)phenoxy]hexyl 4-methylbenzenesulfonate (3a)



3a

250 mL round-bottomed flask was evacuated and refilled with argon (3 times), then under the argon atmosphere 6-[2-(prop-1-en-1-yl)phenoxy]hexan-1-ol (4.00 g, 17.1 mmol) was dissolved in CH_2Cl_2 (60 mL). Then, resulting mixture was cooled down to 0 °C and *p*-toluenesulfonyl chloride (6.65 g, 34.2 mmol) and Et_3N (5.00 mL, 35.9 mmol) were added. The resulting mixture was warmed to room temperature and stirred under argon atmosphere for 16 h. After, resulting mixture was transferred to separatory funnel, diluted with CH_2Cl_2 (60 mL), and washed successively with 1M HCl (100 mL), sat. aq. $NaHCO_3$ (100 mL), and brine (100 mL). Organic phase was collected, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Crude mixture was purified by column chromatography (*n*-hex/AcOEt, 9:1 to 4:1), providing product as a colorless sticky solid (4.85 g, **73%** yield, E/Z = 58:42).

Major isomer (*E*):

R_f = 0.31 (*n*-hex/AcOEt 4:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.2 Hz, 2H), 7.39 (dd, J = 7.6, 1.7 Hz, 1H), 7.34 (ddd, J = 2.5, 1.2, 0.6 Hz, 2H), 7.15 (ddd, J = 8.2, 7.5, 1.7 Hz, 1H), 6.93 – 6.85 (m, 1H), 6.81 (dd, J = 8.2, 1.0 Hz, 1H), 6.69 (dq, J = 15.9, 1.6 Hz, 1H), 6.22 (dq, J = 15.9, 6.6 Hz, 1H), 4.04 (t, J = 6.4 Hz, 2H), 3.93 (t, J = 6.4 Hz, 2H), 2.44 (s, 3H), 1.89 (dd, J = 6.6, 1.8 Hz, 3H), 1.81 – 1.63 (m, 4H), 1.50 – 1.34 (m, 4H).

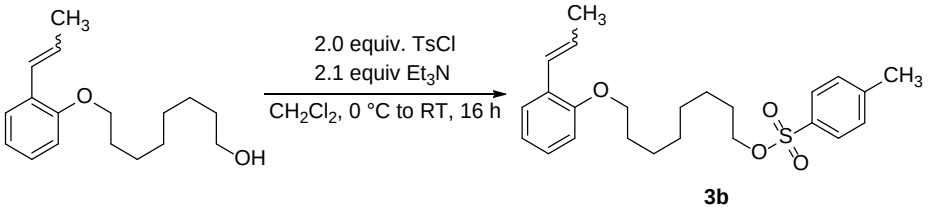
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 144.8, 130.2, 130.0, 128.0, 127.8, 127.2, 126.6, 126.5, 125.7, 120.7, 111.9, 70.6, 68.1, 29.2, 28.9, 25.7, 25.3, 21.8, 19.1.

HRMS (ESI): *m/z* 411.1593 ($[M+Na]^+$, $C_{22}H_{28}O_4SNa^+$ calcd. 411.1606).

EA: Anal. calcd. for $C_{22}H_{28}O_4S$: C, 68.01; H, 7.26; S, 8.25. Found: C, 67.84; H, 7.27; S, 8.38.

FT-IR-ATR: 3058, 3035, 2943, 2863, 1597, 1476, 1355, 1241, 1170, 951, 750 cm^{-1}.

2.4. 8-[2-(Prop-1-en-1-yl)phenoxy]octyl 4-methylbenzenesulfonate (3b)



3b

100 mL round-bottomed flask was evacuated and refilled with argon (3 times), then under the argon atmosphere 8-[2-(prop-1-en-1-yl)phenoxy]octan-1-ol (3.26 g, 12.4 mmol) was dissolved in CH_2Cl_2 (42 mL). Then, resulting mixture was cooled down to 0 °C and *p*-toluenesulfonyl chloride (4.84 g, 24.9 mmol) and Et_3N (3.63 mL, 26.1 mmol) were added. The resulting mixture was warmed to room temperature and stirred under argon atmosphere for 16 h. After, resulting mixture was transferred to separatory funnel, diluted with CH_2Cl_2 (40 mL), and washed successively with 1M HCl (100 mL), sat. aq. $NaHCO_3$ (100 mL), and brine (100 mL). Organic phase was collected, dried over anhydrous $MgSO_4$, filtered, and concentrated. Crude mixture was purified by column chromatography (*n*-hex/AcOEt, 9:1 to 8:2), providing product as a colorless sticky solid (4.03 g, **78%** yield, E/Z = 84:16).

Major isomer (*E*):

R_f = 0.45 (*n*-hex/AcOEt 8:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.41 (dd, J = 7.6, 1.6 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.19 – 7.13 (m, 1H), 6.90 (t, J = 7.1 Hz, 1H), 6.84 (dd, J = 8.2, 0.9 Hz, 1H), 6.73 (dd, J = 15.9, 1.7 Hz, 1H), 6.25 (dq, J = 15.9, 6.6 Hz, 1H), 4.04 (t, J = 6.5 Hz, 2H), 3.97 (t, J = 6.5 Hz, 2H), 2.46 (s, 3H), 1.91 (dd, J = 6.6, 1.7 Hz, 3H), 1.84 – 1.75 (m, 2H), 1.71 – 1.61 (m, 2H), 1.46 (dt, J = 14.9, 6.8 Hz, 2H), 1.39 – 1.25 (m, 6H).

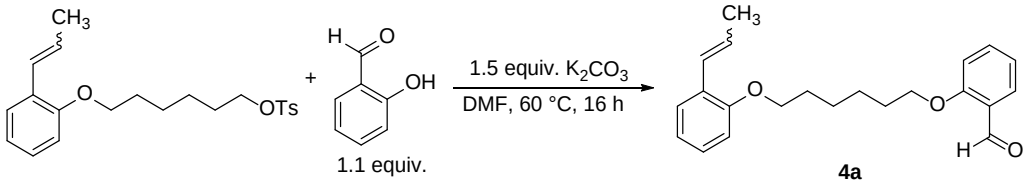
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 144.8, 133.4, 130.0, 128.0, 127.8, 127.2, 126.5, 126.3, 125.8, 120.7, 112.0, 70.8, 68.4, 29.4, 29.3, 29.0, 28.9, 26.1, 25.4, 21.8, 19.1.

HRMS (ESI): *m/z* 417.2094 ($[M+H]^+$, $C_{24}H_{33}O_4S^+$ calcd. 417.2094).

EA: Anal. calcd. for $C_{24}H_{32}O_4S$: C, 69.20; H, 7.74; S, 7.70. Found: C, 69.06; H, 7.68; S, 7.57.

FT-IR-ATR: 3032, 2931, 2856, 1597, 1450, 1357, 1239, 1175, 948, 750 cm^{-1}.

2.5. 2-({6-[2-(Prop-1-en-1-yl)phenoxy]hexyl}oxy)benzaldehyde (4a)



250 mL round-bottomed flask was evacuated and refilled with argon (3 times), then under the argon atmosphere, 6-[2-(prop-1-en-1-yl)phenoxy]hexyl 4-methylbenzenesulfonate (4.30 g, 11.1 mmol) and salicylaldehyde (1.28 mL, 12.2 mmol) were dissolved in anhydrous DMF (40 mL), followed by addition of K_2CO_3 (2.32 g, 16.6 mmol). The resulting mixture was stirred at 60 °C for 16 h, under argon atmosphere. After cooling to RT, Et_2O (80 mL) was added, and the resulting mixture was washed with water (3 x 50 mL), then organic phase was dried over anh. $MgSO_4$, filtered, and volatiles were evaporated *in vacuo*. The crude product was purified by column chromatography (*n*-hex/AcOEt 9:1 to 8:2) and was isolated as a colorless liquid (3.93 g, 91% yield, *E*/*Z* = 58:42).

Major isomer (*E*):

R_f = 0.30 (*n*-hex/AcOEt 8:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 7.84 (dd, J = 7.7, 1.8 Hz, 1H), 7.53 (ddd, J = 8.4, 7.3, 1.9 Hz, 1H), 7.40 (dd, J = 7.6, 1.7 Hz, 1H), 7.16 (ddd, J = 8.2, 7.5, 1.7 Hz, 1H), 7.04 – 6.99 (m, 1H), 6.99 – 6.96 (m, 1H), 6.92 (td, J = 7.5, 0.8 Hz, 1H), 6.84 (dd, J = 8.2, 1.0 Hz, 1H), 6.72 (dq, J = 15.9, 1.6 Hz, 1H), 6.23 (dq, J = 15.9, 6.6 Hz, 1H), 4.10 (t, J = 6.4 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 1.89 (dd, J = 6.6, 1.7 Hz, 3H), 1.94 – 1.82 (m, 4H), 1.63 – 1.54 (m, 4H).

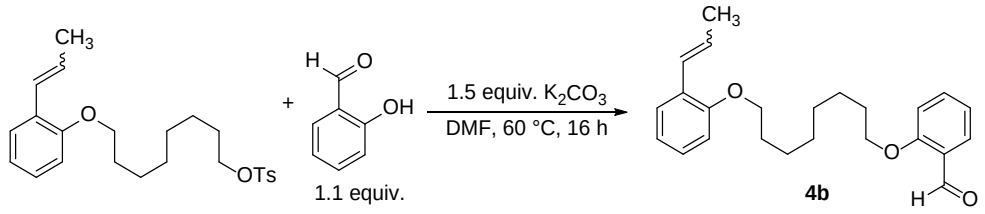
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 161.6, 155.7, 136.0, 128.3, 127.8, 127.1, 126.4, 126.2, 125.7, 124.9, 120.6, 120.6, 112.5, 111.9, 68.4, 68.1, 29.3, 29.1, 26.0, 25.9, 19.1.

HRMS (ESI): *m/z* 361.1778 ($[M+Na]^+$, $C_{22}H_{26}O_3Na^+$ calcd. 361.1780).

EA: Anal. calcd. for $C_{22}H_{26}O_3$: C, 78.07; H, 7.74. Found: C, 77.94; H, 7.99.

FT-IR-ATR: 3075, 3045, 2942, 2856, 1682, 1596, 1452, 1235, 977, 748 cm^{-1}.

2.6. 2-({8-[2-(Prop-1-en-1-yl)phenoxy]octyl}oxy)benzaldehyde (4b)



100 mL round-bottomed flask was evacuated and refilled with argon (3 times), then under the argon atmosphere, 8-[2-(prop-1-en-1-yl)phenoxy]octyl 4-methylbenzenesulfonate (4.00 g, 9.60 mmol) and salicylaldehyde (1.11 mL, 10.6 mmol) were dissolved in anhydrous DMF (35 mL), followed by addition of K_2CO_3 (2.01 g, 14.4 mmol). The resulting mixture was stirred at 60 °C for 16 h, under argon atmosphere. After cooling to RT, Et_2O (70 mL) was added, and the resulting mixture was washed with water (3 x 35 mL), then organic phase was dried over anh. $MgSO_4$, filtered, and volatiles were evaporated *in vacuo*. The crude product was purified by column chromatography (*n*-hex/AcOEt 9:1 to 8:2) and isolated as a colorless solid (3.25 g, **92%** yield, *E*/*Z* = 85:15).

Major isomer (*E*):

R_f = 0.32 (*n*-hex/AcOEt 8:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (d, J = 0.8 Hz, 1H), 7.83 (dd, J = 7.7, 1.8 Hz, 1H), 7.53 (ddd, J = 8.4, 7.3, 1.9 Hz, 1H), 7.39 (dd, J = 7.6, 1.7 Hz, 1H), 7.15 (ddd, J = 8.1, 7.5, 1.7 Hz, 1H), 7.04 – 6.98 (m, 1H), 6.97 (d, J = 8.5 Hz, 1H), 6.88 (td, J = 7.4, 0.7 Hz, 1H), 6.84 (dd, J = 8.2, 1.0 Hz, 1H), 6.72 (dq, J = 15.9, 1.6 Hz, 1H), 6.24 (dq, J = 15.9, 6.6 Hz, 1H), 4.08 (t, J = 6.4 Hz, 2H), 3.98 (t, J = 6.5 Hz, 2H), 1.89 (dd, J = 6.6, 1.8 Hz, 3H), 1.88 – 1.78 (m, 4H), 1.56 – 1.46 (m, 4H), 1.46 – 1.38 (m, 4H).

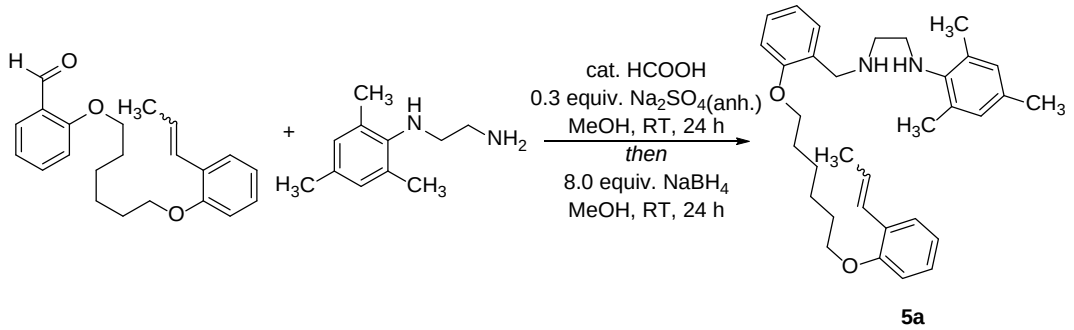
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 161.7, 155.8, 136.1, 128.4, 127.8, 127.2, 126.5, 126.3, 125.9, 125.0, 120.63, 120.62, 112.6, 112.0, 68.6, 68.4, 29.43, 29.41, 29.39, 29.2, 26.24, 26.16, 19.2.

HRMS (ESI): *m/z* 367.2281 ($[M + H]^+$, $C_{24}H_{31}O_3^+$ calcd. 367.2273).

EA: Anal. calcd. for $C_{24}H_{30}O_3$: C, 78.65; H, 8.25. Found: C, 78.62; H, 8.25.

FT-IR-ATR: 3043, 2926, 2854, 1638, 1596, 1450, 1234, 1040, 961, 747 cm^{-1}.

2.7. 2,4,6-Trimethyl-*N*-{2-[({2-[(6-{2-(prop-1-en-1-yl)phenoxy}hexyl)oxy]phenyl}methyl)-amino]ethyl}aniline (5a)



5a

The 100 mL round-bottomed flask was evacuated and refilled with argon (3 times), then 2-({6-[2-(prop-1-en-1-yl)phenoxy]hexyl}oxy)benzaldehyde (5.65 g, 16.7 mmol) was dissolved in anhydrous MeOH (35 mL). After, under argon atmosphere, *N*-mesitylethylenediamine (2.98 g, 16.7 mmol) was added and reaction mixture was stirred at room temperature for 5 minutes, when after Na_2SO_4 (712 mg, 5.01 mmol) and a drop of HCOOH were added. The resulting mixture immediately turned yellow and it was stirred under argon atmosphere at room temperature for 24 h. Next, $NaBH_4$ (5.16 g, 134 mmol) was added in small portions over the period of 30 minutes. After completion of addition the resulting mixture was stirred under argon atmosphere for 24 h. After, 5% aq. NaOH (35 mL) was added, and the MeOH was evaporated *in vacuo*. The resulting aqueous phase was extracted with CH_2Cl_2 (4 x 35 mL) and organic phases were combined, washed with water (50 mL), brine (50 mL), then dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (CH_2Cl_2/MeOH 20:0 to 19:1) to provide the desired product as a colorless dense oil (6.10 g, **73%** yield, *E*/*Z* 56:44).

Major isomer (*E*):

R_f = 0.28 (CH_2Cl_2/MeOH 19:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, J = 7.6, 1.7 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.18 – 7.13 (m, 1H), 6.95 – 6.83 (m, 4H), 6.81 (s, J = 3.4 Hz, 2H), 6.72 (dd, J = 15.9, 1.7 Hz, 1H), 6.24 (dq, J = 15.9, 6.6 Hz, 1H), 4.01 (t, J = 6.4 Hz, 2H), 3.96 (t, J = 6.5 Hz, 2H), 3.85 (s, 2H), 3.06 – 3.02 (m, 2H), 2.81 – 2.77 (m, 2H), 2.26 (s, 6H), 2.22 (s, 3H), 1.89 (dd, J = 6.6, 1.7 Hz, 3H), 1.87 – 1.78 (m, 4H), 1.60 – 1.50 (m, 4H).

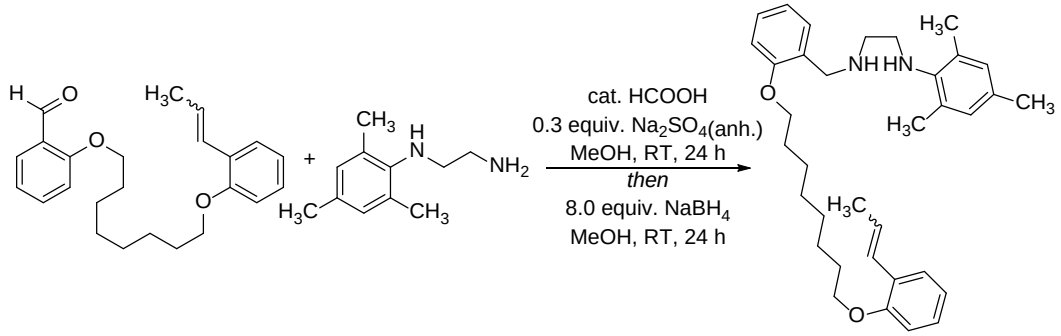
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 155.7, 144.0, 131.1, 129.7, 129.5, 128.5, 128.3, 127.8, 127.2, 126.58, 126.55, 126.5, 126.3, 125.8, 120.6, 120.3, 111.9, 111.1, 68.2, 67.8, 49.1, 48.4, 29.42, 29.35, 26.11, 26.07, 20.7, 19.1, 18.6.

HRMS (ESI): *m/z* 501.3484 ($[M + H]^+$, $C_{33}H_{45}N_2O_2^+$ calcd. 501.3481).

EA: Anal. calcd. for $C_{33}H_{44}N_2O_2$: C, 79.16; H, 8.86; N, 5.59. Found: C, 79.18; H, 8.82; N, 5.71.

FT-IR-ATR: 3348, 3033, 2931, 1597, 1451, 1236, 1113, 1027, 853, 748 cm^{-1}.

2.8. 2,4,6-Trimethyl-*N*-{2-[({2-[(8-{2-(prop-1-en-1-yl)phenoxy}octyl)oxy]phenyl}methyl)-amino]ethyl}aniline (5b)



5b

The 100 mL round-bottomed flask was evacuated and refilled with argon (3 times), then 2-({8-[2-(prop-1-en-1-yl)phenoxy]octyl}oxy)benzaldehyde (1.10 g, 3.00 mmol) was dissolved in anhydrous MeOH (13 mL). After, under argon atmosphere, *N*-mesitylethylenediamine (535 mg, 3.00 mmol) was added and the reaction mixture was stirred at room temperature for 5 minutes, when after Na_2SO_4 (128 mg, 0.90 mmol) and a drop of HCOOH were added. The resulting mixture immediately turned yellow and it was stirred under argon atmosphere at room temperature for 24 h. Next, $NaBH_4$ (926 mg, 24.0 mmol) was added in small portions over the period of 30 minutes. After completion of addition the resulting mixture was stirred under argon atmosphere for 24 h. After, 5% aq. NaOH (13 mL) was added, and the MeOH was evaporated *in vacuo*. The resulting aqueous phase was extracted with CH_2Cl_2 (4 x 20 mL) and organic phases were combined, washed with water (20 mL), brine (20 mL), then dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (CH_2Cl_2/MeOH 20:0 to 19:1) to provide the desired product as a colorless dense oil (977 mg, **62%** yield, *E*/*Z* 85:15).

Major isomer (*E*):

R_f = 0.23 (CH_2Cl_2/MeOH 19:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 7.6, 1.7 Hz, 1H), 7.26 (d, J = 7.6 Hz, 1H), 7.24 (dd, J = 7.8, 1.9 Hz, 1H), 7.19 – 7.14 (m, 1H), 6.96 – 6.84 (m, 4H), 6.83 – 6.81 (m, 2H), 6.75 (dd, J = 15.9, 1.7 Hz, 1H), 6.26 (dq, J = 15.9, 6.6 Hz, 1H), 4.00 (t, J = 6.4 Hz, 2H), 3.98 (t, J = 6.5 Hz, 2H), 3.88 (s, 2H), 3.08 – 3.04 (m, 2H), 2.84 – 2.80 (m, 2H), 2.28 (s, 6H), 2.24 (s, 3H), 1.92 (dd, J = 6.6, 1.7 Hz, 3H), 1.85 – 1.78 (m, 4H), 1.55 – 1.45 (m, 4H), 1.44 – 1.36 (m, 4H).

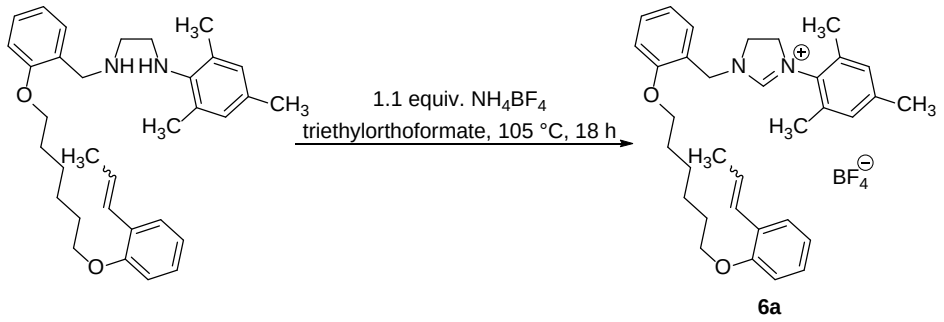
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 155.8, 143.9, 131.2, 130.0, 129.8, 129.5, 128.4, 128.0, 127.8, 127.2, 126.5, 126.2, 125.8, 120.6, 120.3, 112.0, 111.2, 72.7, 70.5, 68.4, 67.9, 49.2, 49.0, 48.2, 29.45, 29.39, 26.28, 26.23, 20.7, 19.1, 18.6.

HRMS (ESI): *m/z* 529.3791 ($[M + H]^+$, $C_{35}H_{49}N_2O_2^+$ calcd. 529.3789).

EA: Anal. calcd. for $C_{35}H_{48}N_2O_2$: C, 79.50; H, 9.15; N, 5.30. Found: C, 79.51; H, 9.09; N, 5.32.

FT-IR-ATR: 3348, 3032, 2931, 2854, 1597, 1452, 1237, 1113, 1027, 853, 747 cm^{-1}.

2.9. 3-({2-[(6-{2-[Prop-1-en-1-yl]phenoxy}hexyl)oxy]phenyl}methyl)-1-(2,4,6-trimethyl-phenyl)-4,5-dihydro-1λ5-imidazol-1-ylium tetrafluoroborate (6a)



6a

To a 20 mL vial was added 2,4,6-trimethyl-N-{2-[({2-[(6-{2-[(prop-1-en-1-yl]phenoxy}hexyl)oxy]phenyl}methyl)amino]ethyl}aniline (1001 mg, 2.00 mmol) and triethyl orthoformate (6.8 mL, 40.0 mmol), followed by NH_4BF_4 (238 mg, 2.20 mmol). The vial was closed with a screw cap, needle was put in the septum, and the reaction mixture was heated to 105 °C for 16 h. Next, the reaction mixture was cooled to room temperature and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography (DCM/MeOH 1:0 to 97:3) providing product as a yellowish foamy solid (921 mg, **77%** yield, *E*/*Z* 4:1).

Major isomer (*E*):

R_f = 0.18 (CH_2Cl_2/MeOH 19:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.41 (dd, J = 7.4, 1.3 Hz, 1H), 7.37 (ddd, J = 8.3, 2.5, 1.2 Hz, 2H), 7.17 – 7.12 (m, 1H), 6.99 (td, J = 7.5, 0.8 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 6.90 (s, 2H), 6.90 – 6.86 (m, 1H), 6.82 (dd, J = 8.2, 0.9 Hz, 1H), 6.70 (dq, J = 15.9, 1.4 Hz, 1H), 6.21 (dq, J = 15.9, 6.6 Hz, 1H), 4.83 (s, 2H), 4.13 – 4.07 (m, 4H), 4.04 (t, J = 6.8 Hz, 2H), 3.95 (t, J = 6.3 Hz, 2H), 2.25 (s, 3H), 2.23 (s, 6H), 1.85 (ddd, J = 14.9, 6.9, 1.8 Hz, 3H), 1.85 – 1.73 (m, 4H), 1.58 – 1.44 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 156.5, 155.7, 140.4, 135.5, 131.9, 131.2, 130.6, 130.1, 130.0, 127.9, 127.0, 126.4, 126.2, 125.7, 121.3, 120.6, 111.8, 111.7, 68.5, 68.1, 51.0, 48.6, 48.2, 29.22, 29.17, 26.0, 25.8, 21.1, 17.5, 14.8.

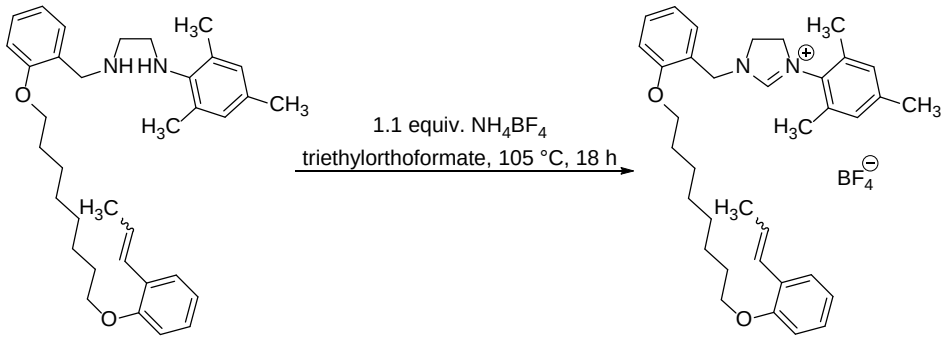
^{19}F NMR (376 MHz, $CDCl_3$) δ -152.61 (dd, J = 1.2 Hz).

HRMS (ESI): *m/z* 511.3338 ($[M - BF_4]^+$, $C_{34}H_{43}N_2O_2^+$ calcd. 511.3325).

EA: Anal. calcd. for $C_{34}H_{43}BF_4N_2O_2$: C, 68.28; H, 7.24; F, 12.70; N, 4.68. Found: C, 68.16; H, 7.44; F, 12.61; N, 4.57.

FT-IR-ATR: 3063, 2942, 2862, 1642, 1489, 1265, 1052, 856, 732, 702 cm^{-1}.

2.10. 3-({2-[(8-{2-[Prop-1-en-1-yl]phenoxy}octyl)oxy]phenyl}methyl)-1-(2,4,6-trimethyl-phenyl)-4,5-dihydro-1λ5-imidazol-1-ylium tetrafluoroborate (6b)



6b

To a 20 mL round-bottomed flask was added 2,4,6-trimethyl-N-{2-[({2-[(8-{2-[(prop-1-en-1-yl]phenoxy}oc-tyl)oxy]phenyl}methyl)amino]ethyl}aniline (952 mg, 1.80 mmol) and triethyl orthoformate (12.2 mL, 72.0 mmol), followed by NH_4BF_4 (214 mg, 1.98 mmol). The reaction mixture was heated to 105 °C for 16 h. Next, the reaction mixture was cooled to room temperature and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography (DCM/MeOH 1:0 to 97:3) and further by crystallization from MeOH/Et_2O mixture providing the desired product as a colorless amorphous solid (1052 mg, **93%** yield, *E*/*Z* 9:1).

Major isomer (*E*):

R_f = 0.19 (CH_2Cl_2/MeOH 19:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.43 – 7.34 (m, 2H), 7.17 – 7.11 (m, 1H), 6.99 (t, J = 7.2 Hz, 1H), 6.91 (s, 2H), 6.94 – 6.81 (m, 3H), 6.71 (dd, J = 15.9, 1.5 Hz, 1H), 6.23 (dq, J = 16.0,

6.6 Hz, 1H), 4.83 (s, 2H), 4.17 – 4.05 (m, 4H), 4.01 (t, J = 6.9 Hz, 2H), 3.95 (t, J = 6.5 Hz, 2H), 2.27 (s, 3H), 2.23 (s, 6H), 1.89 (dd, J = 6.6, 1.6 Hz, 3H), 1.86 – 1.72 (m, 4H), 1.53 – 1.26 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 157.4, 155.8, 140.5, 135.6, 132.1, 131.2, 130.6, 130.1, 127.9, 127.2, 126.5, 126.2, 125.9, 121.4, 120.69, 120.66, 112.1, 111.9, 68.7, 68.3, 51.1, 48.7, 48.4, 29.38, 29.36, 29.33, 26.2, 26.1, 21.1, 19.1, 17.6.

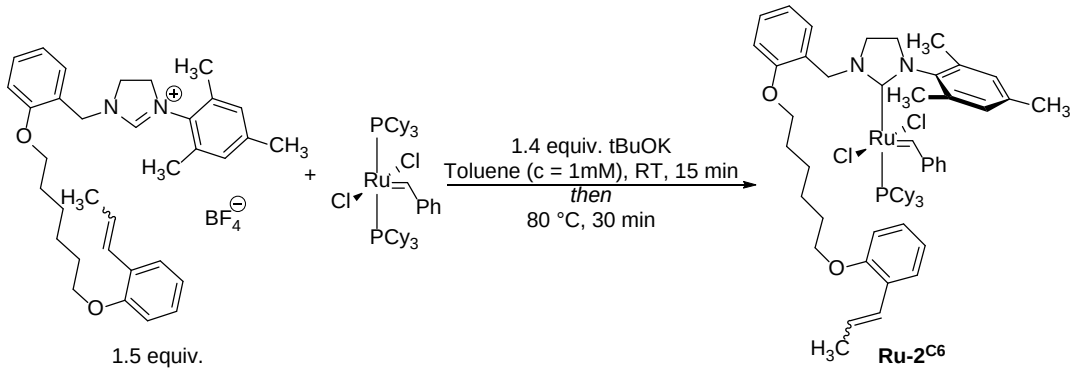
^{19}F NMR (376 MHz, $CDCl_3$) δ -152.29 (s).

HRMS (ESI): *m/z* 539.3639 ($[M - BF_4]^+$, $C_{36}H_{47}N_2O_2^+$ calcd. 539.3638).

EA: Anal. calcd. for $C_{34}H_{43}BF_4N_2O_2$: C, 69.01; H, 7.56; F, 12.13; N, 4.47. Found: C, 68.86; H, 7.63; F, 12.30; N, 4.69.

FT-IR-ATR: 3090, 3034, 2933, 2856, 1634, 1590, 1449, 1242, 1052, 970, 755 cm^{-1}.

2.11. Benzylidene(dichloro)(1-{[2-({6-[2-(prop-1-en-1-yl)phenoxy]hexyl}oxy)phenyl]methyl}-3-[2,4,6-trimethylphenyl]imidazolidin-2-ylidene)ruthenium (Ru-2^{C6})



Oven dried Schlenk vessel was evacuated and refilled with argon (3 times). After, 3-({2-[(6-{2-[prop-1-en-1-yl]phenoxy}hexyl)oxy]phenyl}methyl)-1-(2,4,6-trimethylphenyl)-4,5-dihydro-1λ5-imidazol-1-ylium tetrafluoroborate (135 mg, 225 μmol) was added followed by the addition of anh. toluene (15 mL). Next, *t*BuOK (23.6 mg, 210 μmol) was added and the reaction mixture was stirred at RT for 15 minutes, to generate "*t*-butanolate adduct". Next, (benzylidene)bis(tricyclohexylphosphine)dichlororuthenium pre-catalyst (127 mg, 150 μmol) was added in one portion and the reaction mixture was immediately placed in preheated oil bath (80 °C). After 30 minutes TLC has shown full consumption of **Gru-1** pre-catalyst and formation of new complex. The reaction mixture was cooled down to 0 °C, transferred on column chromatography, and eluted with *n*-hex/AcOEt (9:1, then 8:2). Fraction with newly formed

complex were collected and evaporated. Crude pre-catalyst was dispersed in *n*-pentane, sonicated for few minutes and placed in freezer (-20 °C) for 20 h. Liquid was decantated and remaining solid was dried *in vacuo* providing red amorphous solid (78 mg, 49% yield).

Major isomer (*E*):

R_f = 0.38 (*n*-hex/AcOEt 8:2)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 18.90 (s, 1H), 8.03 (d, J = 6.4 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.34 – 7.22 (m, 2H), 7.17 – 7.08 (m, 4H), 7.02 (t, J = 7.4 Hz, 1H), 6.95 (d, J = 8.3 Hz, 1H), 6.92 – 6.82 (m, 4H), 6.72 (dd, J = 15.9, 1.5 Hz, 1H), 6.24 (ddd, J = 15.8, 13.2, 6.6 Hz, 1H), 5.42 (s, 2H), 4.06 (t, J = 6.6 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 3.70 (s, 4H), 2.31 (d, J = 9.9 Hz, 3H), 2.39 – 2.24 (m, 2H), 2.25 – 2.07 (m, 4H), 1.89 (d, J = 2.3 Hz, 6H), 1.87 (d, J = 1.6 Hz, 3H), 1.97 – 1.78 (m, 2H), 1.67 – 1.45 (m, 18H), 1.24 (dd, J = 24.5, 12.1 Hz, 6H), 1.07 (dd, J = 23.9, 11.5 Hz, 6H), 1.00 – 0.89 (m, 3H).

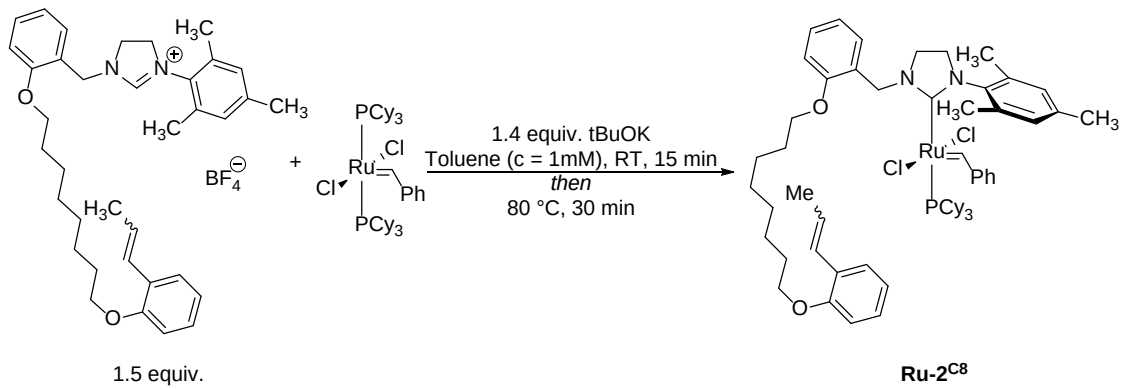
^{13}C NMR (101 MHz, CD_2Cl_2) δ 219.0 (d, J = 74.1 Hz), 157.8, 156.3, 151.5, 138.0, 137.4, 137.0, 131.4, 130.9, 129.6, 129.3, 129.0, 128.6, 128.2, 127.5, 126.7, 126.6, 126.3, 126.2, 124.0, 121.1, 120.9, 112.5, 111.6, 68.8, 68.7, 54.4, 51.7, 49.1 (d, J = 3.2 Hz), 48.6, 35.8 (d, J = 60.8 Hz), 31.8 (d, J = 15.8 Hz), 29.9, 28.3 (d, J = 10.0 Hz), 26.9, 26.6, 21.2, 19.3, 18.7.

^{31}P NMR (162 MHz, CD_2Cl_2) δ 35.2 (s).

HRMS (ESI): *m/z* 1051.4373 ([M - H]$^+$, $C_{59}H_{80}Cl_2N_2O_2PRu^+$ calcd. 1051.4378).

FT-IR-ATR: 3057, 2923, 2849, 1738, 1569, 1446, 1238, 1004, 896, 749 cm^{-1}.

2.12. Benzylidene(dichloro)(1-{[2-({8-[2-(prop-1-en-1-yl)phenoxy]octyl}oxy)phenyl]methyl}-3-[2,4,6-trimethylphenyl]imidazolidin-2-ylidene)ruthenium (Ru-2^{C8})



Oven dried Schlenk vessel was evacuated and refilled with argon (3 times). After, 3-({2-[(6-{2-[prop-1-en-1-yl]phenoxy}octyl)oxy]phenyl}methyl)-1-(2,4,6-trimethylphenyl)-4,5-dihydro-1λ5-imidazol-1-ylium tetrafluoroborate (141 mg, 225 μmol) was added follow by addition of anh. toluene (15 mL). Next, *t*BuOK (23.6 mg, 210 μmol) was added and the reaction mixture was stirred at RT for 15 minutes, to generate "*t*-butanolate adduct". Next, (benzylidene)bis(tricyclohexylphosphine)dichlororuthenium pre-catalyst (127 mg, 150 μmol) was added in one portion and the reaction mixture was immediately placed in preheated oil bath (80 °C). After 30 minutes TLC has shown full consumption of **Gru-1** pre-catalyst and formation of new complex. The reaction mixture was cooled down to 0 °C, transferred on column chromatography, and eluted with *n*-hex/AcOEt (9:1, then 8:2). Fraction with newly formed complex were collected, evaporated, and dried *in vacuo* providing red amorphous solid (70 mg, 43% yield).

Major isomer (*E*):

R_f = 0.41 (*n*-hex/AcOEt 8:2).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 18.90 (s, 1H), 8.03 (dd, J = 7.5, 1.5 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.34 – 7.29 (m, 1H), 7.17 – 7.10 (m, 3H), 7.03 (td, J = 7.4, 0.8 Hz, 1H), 6.95 (d, J = 8.3 Hz, 1H), 6.89 – 6.84 (m, 2H), 6.73 (dd, J = 15.9, 1.7 Hz, 1H), 6.25 (dq, J = 15.9, 6.6 Hz, 1H), 5.42 (s, 2H), 4.05 (t, J = 6.6 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 3.71 (s, J = 27.6 Hz, 4H), 2.38 – 2.26 (m, 5H), 2.26 – 2.09 (m, 4H), 1.90 (s, J = 1.6 Hz, 6H), 1.88 (d, J = 1.7 Hz, 3H), 1.87 – 1.81 (m, 2H), 1.64 – 1.42 (m, 18H), 1.36 – 1.18 (m, 10H), 1.08 (dd, J = 24.5, 12.1 Hz, 6H), 1.01 – 0.91 (m, 3H).

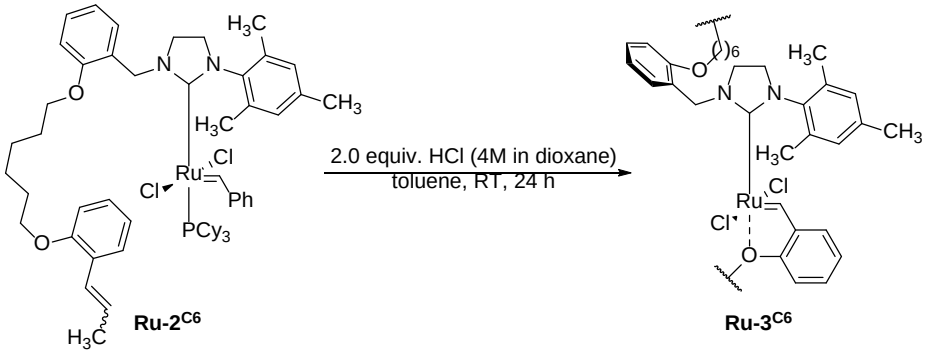
^{13}C NMR (101 MHz, CD_2Cl_2) δ 293.7 (dd, J = 25.3, 4.7 Hz), 219.0 (d, J = 74.1 Hz), 157.8, 156.3, 151.4 (d, J = 1.4 Hz), 138.0, 137.4, 137.0 (d, J = 0.4 Hz), 131.3, 130.9, 129.6, 129.3, 128.6, 128.23, 128.20, 127.5, 126.7, 126.5, 126.2, 123.9, 121.0, 120.9, 112.4, 111.6, 68.9, 68.7, 51.7 (d, J = 2.2 Hz), 49.1 (d, J = 3.3 Hz), 48.6, 34.7, 31.8, 31.7, 29.93 (d, J = 4.9 Hz), 29.86 (d, J = 6.4 Hz), 28.3 (d, J = 10.0 Hz), 26.9 (d, J = 5.8 Hz), 26.7 (d, J = 1.0 Hz), 22.9, 21.2, 19.3, 18.7, 14.4.

^{31}P NMR (162 MHz, CD_2Cl_2) δ 35.2 (s).

HRMS (ESI): *m/z* 1079.4696 ($[M - H]^+$, $C_{61}H_{84}Cl_2N_2O_2PRu^+$ calcd. 1079.4686).

FT-IR-ATR: 3057, 2924, 2850, 1738, 1446, 1239, 1112, 1005, 896, 748 cm^{-1}.

2.13. Polymeric complex Ru-3^{C6}

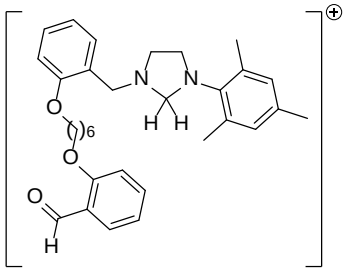


Oven dried Schlenk vessel was evacuated and refilled with argon (3 times). After, benzylidene(dichloro)(1-{[2-({6-[2-(prop-1-en-1-yl)phenoxy]hexyl}oxy)phenyl]methyl}-3-[2,4,6-trimethyl-phenyl]imidazolidin-2-ylidene)ruthenium (137 mg, 130 μmol) was added follow by addition of anh. toluene (13 mL). Next, 4M solution of HCl in dioxane (65 μL, 260 μmol) was added and the resulting mixture was stirred at room temperature for 24 h. After, the resulting mixture was collected to the syringe and filtered through syringe filter (PTFE, 0.45 μm) to remove precipitated tricyclohexylphosphonium chloride. The filtrate was concentrated and dried *in vacuo* providing the desired polymeric complex as a brown amorphous solid (69 mg, 81% yield).

^{1}H NMR[1] (400 MHz, CD_2Cl_2) δ 16.26 – 16.17 (m, 1H).

^{13}C NMR[2] (101 MHz, CD_2Cl_2) δ 290.4.

MS (MALDI-TOF): *m/z* 500.1 ([M]$^+$, $C_{27}H_{30}N_2O_3^+$ calcd. 500.3) which corresponds to following molecule:

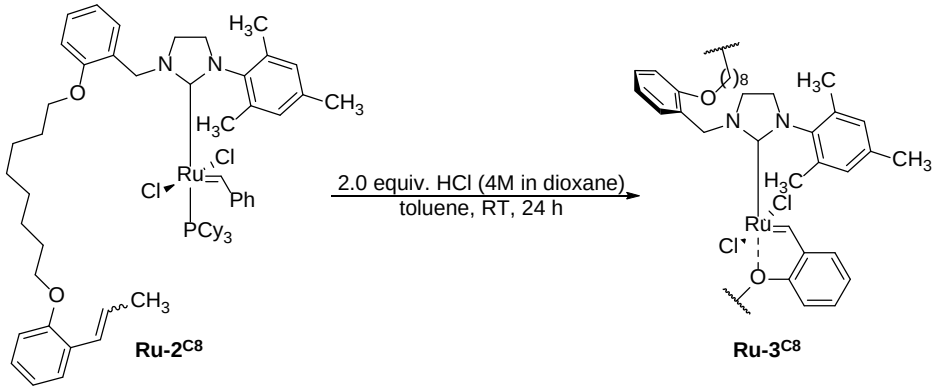


FT-IR-ATR: 3069, 2926, 2852, 1943, 1590, 1450, 1236, 1108, 1004, 850, 751 cm^{-1}.

[1] Due to polymeric structure of compound the obtained spectrum resulted in inconsistent data of integrals, thus only benzylidene proton peak was reported.

[2] Due to polymeric structure of compound the obtained spectrum has got very low insensitivity, thus only benzylidene carbon peak was reported, based on HSQC experiment.

2.14. Polymeric complex Ru-3^{C8}

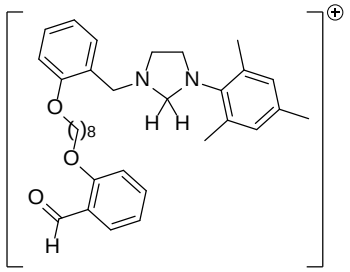


Oven dried Schlenk vessel was evacuated and refilled with argon (3 times). After, benzylidene(dichloro)(1-{[2-({8-[2-(prop-1-en-1-yl)phenoxy]octyl}oxy)phenyl]methyl}-3-[2,4,6-trimethyl-phenyl]imidazolidin-2-ylidene)ruthenium (70 mg, 64.7 μmol) was added follow by addition of anh. toluene (6.5 mL). Next, 4M solution of HCl in dioxane (32.4 μL, 129 μmol) was added and the resulting mixture was stirred at room temperature for 24 h. After, the resulting mixture was collected to the syringe and filtered through syringe filter (PTFE, 0.45 μm) to remove precipitated tricyclohexylphosphonium chloride. The filtrate was concentrated and dried *in vacuo* providing the desired polymeric complex as a brown amorphous solid (43 mg, 97% yield).

^{1}H NMR[3] (400 MHz, CD_2Cl_2) δ 16.16 (s, 1H).

^{13}C NMR[4] (101 MHz, CD_2Cl_2) δ 290.4.

MS (MALDI-TOF): *m/z* 528.2 ($[M]^+$, $C_{27}H_{30}N_2O_3^+$ calcd. 528.3) which corresponds to following molecule:



FT-IR-ATR: 3065, 2925, 2852, 1937, 1647, 1452, 1238, 1107, 1045, 852, 750 cm^{-1}.

[3] Due to polymeric structure of compound the obtained spectrum resulted in inconsistent data of integrals, thus only benzylidene proton peak was reported.

[4] Due to polymeric structure of compound the obtained spectrum has got very low insensitivity, thus only benzylidene carbon peak was reported, based on HSQC experiment.

3. Catalytic activity studies

3.1. Reaction course plots

Oven dried Schlenk vessel was evacuated and refilled with argon (3 times). After, diethyl diallylmalonate (123 μL, 500 μmol) and 1,2,4,5-tetramethylbenzene (67.8 mg, 500 μmol) were added follow by addition of anh. toluene (5 mL). Small sample of the mixture (ca. 50 μL) was aliquoted as a "sample zero". Next, the corresponding ruthenium complex **Ru-3^{C6}** or **Ru-4** (1 mol%, 5.0 μmol) was added in one portion to the reaction mixture and the vessel was immediately placed in preheated oil bath (40, 60 or 80 °C). The samples were aliquoted in time intervals and measured using GC. The conversion was calculated based on substrate/internal standard ratio of peak area using following equation:

$$Conv[\%] = \left(1 - \frac{[A_{subs}]^{t} \cdot [A_{IS}]^{t=0}}{[A_{subs}]^{t=0} \cdot [A_{IS}]^{t}}\right) \cdot 100$$

Equation 1. Equation of conversion determined using GC analysis. $[A_{subs}]^{t}$ – area of substrate peak at certain time; $[A_{subs}]^{t=0}$ – area of substrate peak at "time zero"; $[A_{IS}]^{t}$ – area of internal standard (1,2,4,5-tetramethylbenzene) peak at certain time; $[A_{IS}]^{t=0}$ – area of internal standard (1,2,4,5-tetramethylbenzene) peak at "time zero".

GC data of experiments:

Table S1. Gas chromatography data. A_{IS} – area of internal standard signal; A_{subs} – area of substrate signal; nd – not detected.

temp. = 40 °C							
Ru-4				**Ru-3^{C6}**			
Time [min]	A_{IS}	A_{subs}	Conv. [%]	Time [min]	A_{IS}	A_{subs}	Conv. [%]
0	96826	99827	-	0	114942	108044	-
15	126807	9557	92.7	15	122701	89839	22.1
30	245222	14032	94.9	30	200932	138676	26.6
60	238567	9849	96.0	60	243516	134365	41.3
120	275166	8139	97.1	120	310181	106121	63.6
240	310913	6361	98.0	240	164517	27943	81.9
360	140794	2423	98.3	360	151564	20112	85.9

temp. = 60 °C							
Ru-4				**Ru-3^{C6}**			
Time [min]	A_{IS}	A_{subs}	Conv. [%]	Time [min]	A_{IS}	A_{subs}	Conv. [%]
0	144277	137759	-	0	114495	115013	-
15	124842	1109	99.1	15	121691	59098	51.7
30	229135	982	99.6	30	236365	94687	60.1
60	317479	988	99.7	60	275613	65806	76.2
120	309669	914	99.7	120	305245	23014	92.5
240	372752	739	99.8	240	188109	2533	98.7
360	6553.22	55.67	99.1	360	126647	865	99.3

temp. = 80 °C							
Ru-4				**Ru-3^{C6}**			
Time [min]	A_{IS}	A_{subs}	Conv. [%]	Time [min]	A_{IS}	A_{subs}	Conv. [%]
0	185966	190570	-	0	308475	339218	-
5	192044	1316	99.3	5	235121	66689	74.2
10	223712	582	99.7	10	306287	44106	86.9
15	260977	242	99.9	15	164355	15015	91.7
30	177460	126	99.9	30	141438	5282	96.6
60	151972	nd	100.0	60	198325	2935	98.7
120	117177	nd	100.0	120	103596	560	99.5
240	22425	nd	100.0	240	292547	529	99.8
360	331942	nd	100.0	360	308640	212	99.9

3.2. Recycling of polymeric ruthenium complexes

Oven dried Schlenk vessel was evacuated and refilled with argon (3 times). After, diethyl diallylmalonate (1233 μL, 5.0 mmol) and 1,2,4,5-tetramethylbenzene (678 mg, 5.0 mmol) were added follow by addition of anh. toluene (25 mL). Small sample of the mixture (ca. 50 μL) was aliquoted as a "sample zero". Next, the ruthenium complex **Ru-3^{C6}** (32.7 mg, 0.05 mmol. 1 mol%) was added in one portion to the reaction mixture and the vessel was immediately placed in preheated oil bath (80 °C). After 2 hours the sample for GC analysis was taken and the resulting mixture was concentrated *in vacuo* to dryness. 10 mL of *n*-pentane was added to precipitate polymeric ruthenium complex. After centrifugation, the liquid was decantated (it was repeated 4 more times). The remaining polymeric complex was dried *in vacuo* overnight and used in the next run. The next run was re-scaled based on the amount of recovered catalyst (Table S2). The conversion was calculated using Equation 1 (Table S3).

Table S2. Setup of recycling reactions with reagent amounts.

Run	Scale [mmol]	**Ru-3^{C6}** [mg]	DEDAM [μL]	IS [mg]	Toluene [mL]	Conv. [%]	Yield of recycled **Ru-3^{C6}** [%]
1	5.00	32.7	1233	678.0	25.0	>99	38%
2	1.91	12.5	471.0	259.0	9.55	95	66%
3	1.27	8.3	313.2	172.2	6.35	57	

Table S3. Gas chromatography data. A_{IS} – area of internal standard signal; A_{subs} – area of substrate signal.

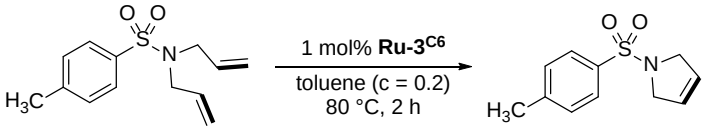
Run 1			
Time [min]	A_{IS}	A_{subs}	Conv. [%]
0	140774	168516	-
120	164683	850	99.6
Run 2			
Time [min]	A_{IS}	A_{subs}	Conv. [%]
0	282907	316837	-
120	175684	10229	94.8
Run 3			
Time [min]	A_{IS}	A_{subs}	Conv. [%]
0	303268	321662	-
120	469530	212691	57.3

4. RCM experiments and products analysis

4.1. General procedure of RCM reactions

Oven dried Schlenk vessel was evacuated and refilled with argon (3 times). Then substrate and anhydrous toluene was added. Next, ruthenium complex was added in one portion, reaction vessel was placed in preheated oil bath (80 °C), and the reaction mixture was stirred upon certain time. After the reaction mixture was cooled down to room temperature, transferred to round-bottom flask, and all the volatiles were removed *in vacuo*. The resulting crude mixture was purified by column chromatography on silica or by precipitation.

4.2. 1-Tosyl-2,5-dihydro-1*H*-pyrrole (8b)



7b **8b**

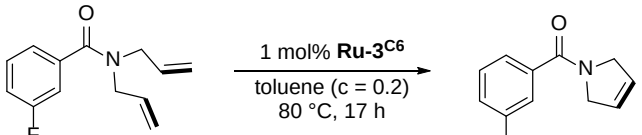
The reaction was set up based on general procedure in 1.0 mmol scale using *N,N*-diallyltosylamide (**7b**) (251 mg, 1.0 mmol), **Ru-3^{C6}** complex (6.55 mg, 0.01 mmol) in toluene (5 mL) for 2 h at 80 °C. The product was purified by column chromatography (SiO_2, *n*-hex/AcOEt 17:3) providing the desired product **8b** as a colorless solid (212 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.35 – 7.28 (m, 2H), 5.66 – 5.63 (m, 2H), 4.13 – 4.10 (m, 4H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 134.4, 129.9, 127.5, 125.6, 55.0, 21.7.

Spectral data are in accordance to the literature.[3]

4.3. (2,5-Dihydro-1*H*-pyrrol-1-yl)(3-fluorophenyl)methanone (8c)



7c **8c**

The reaction was set up based on general procedure in 1.0 mmol scale using *N,N*-diallyl-3-fluorobenzamide (**7c**) (219 mg, 1.0 mmol), **Ru-3^{C6}** complex (6.55 mg, 0.01 mmol) in toluene (5 mL) for 17 h at 80 °C. The product was purified by column chromatography (SiO_2, *n*-hex/AcOEt 19:1 to 3:1) providing the desired product **8c** as a colorless liquid (86 mg, 45% yield).

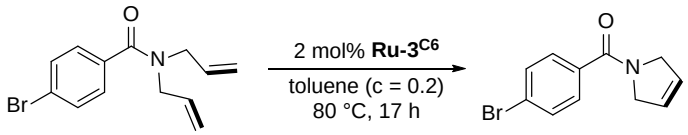
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 1H), 7.30 (dt, J = 7.6, 1.3 Hz, 1H), 7.23 (ddd, J = 9.0, 2.6, 1.5 Hz, 1H), 7.12 (tdd, J = 8.4, 2.6, 1.1 Hz, 1H), 5.94 – 5.88 (m, 1H), 5.78 – 5.71 (m, 1H), 4.44 (ddd, J = 5.8, 4.0, 2.1 Hz, 2H), 4.20 (ddd, J = 5.8, 4.0, 2.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5 (d, J = 2.4 Hz), 162.6 (d, J = 247.8 Hz), 138.9 (d, J = 6.9 Hz), 130.4 (d, J = 8.0 Hz), 126.1, 125.2, 122.7 (d, J = 3.2 Hz), 117.1 (d, J = 21.1 Hz), 114.27 (d, J = 22.8 Hz), 55.9, 53.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.0 (td, J = 8.8, 5.6 Hz).

Spectral data are in accordance to the literature.[4]

4.4. (2,5-Dihydro-1*H*-pyrrol-1-yl)(4-bromophenyl)methanone (8d)



7d **8d**

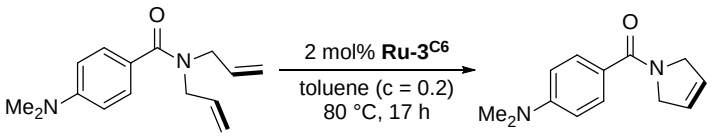
The reaction was set up based on general procedure in 0.5 mmol scale using *N,N*-diallyl-4-bromobenzamide (**7d**) (140 mg, 0.5 mmol), **Ru-3^{C6}** complex (6.55 mg, 0.01 mmol) in toluene (2.5 mL) for 17 h at 80 °C. The product was purified by column chromatography (SiO_2, *n*-hex/AcOEt 9:1 to 3:1) providing the desired product **8d** as an off-white solid (75 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.43 – 7.38 (m, 2H), 5.91 (dp, J = 6.4, 2.1 Hz, 1H), 5.74 (dp, J = 6.3, 2.1 Hz, 1H), 4.44 (ddd, J = 6.1, 4.1, 2.1 Hz, 2H), 4.19 (ddd, J = 6.1, 4.1, 2.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 135.7, 131.8, 128.7, 126.2, 125.2, 124.4, 55.9, 53.6.

Spectral data are in accordance to the literature.[5]

4.5. (2,5-Dihydro-1*H*-pyrrol-1-yl)[4-(dimethylamino)phenyl]methanone (8e)



7e **8e**

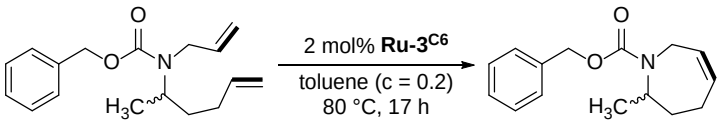
The reaction was set up based on general procedure in 0.5 mmol scale using *N,N*-diallyl-4-(dimethylamino)benzamide (**7e**) (122 mg, 0.5 mmol), **Ru-3^{C6}** complex (6.55 mg, 0.01 mmol) in toluene (2.5 mL) for 17 h at 80 °C. The product was purified by column chromatography (SiO_2, *n*-hex/AcOEt 7:3 to 4:6) providing the desired product **8e** as an off-white solid (77 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 6.70 – 6.64 (m, 2H), 5.89 (br s, 1H), 5.76 (br s, 1H), 4.45 (br s, 2H), 4.34 (br s, 2H), 3.00 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 151.6, 129.2, 126.2, 125.4, 123.8, 111.1, 56.1, 53.8, 40.3.

Spectral data are in accordance to the literature.[9]

4.6. Benzyl 2-methyl-2,3,4,7-tetrahydro-1*H*-azepine-1-carboxylate (8f)



7f **8f**

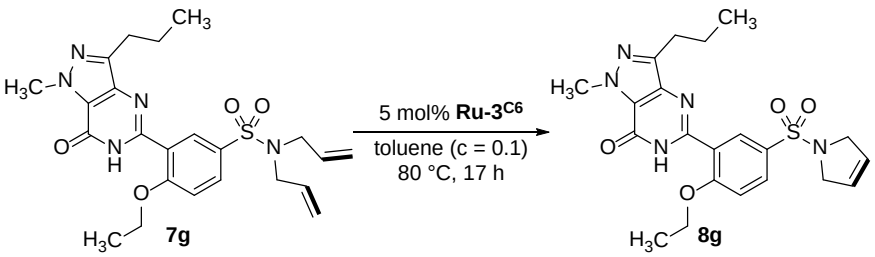
The reaction was set up based on general procedure in 0.5 mmol scale using benzyl allyl(hex-5-en-2-yl)carbamate (**7f**) (137 mg, 0.5 mmol), **Ru-3^{C6}** complex (6.55 mg, 0.01 mmol) in toluene (2.5 mL) for 17 h at 80 °C. The product was purified by column chromatography (SiO_2, *n*-hex/AcOEt 9:1 to 6:4) providing the desired product **8f** as a colorless liquid (119 mg, 97% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H), 5.75 – 5.61 (m, 2H), 5.14 (dd, J = 7.0, 2.6 Hz, 2H), 4.48 – 4.22 (m, 1H), 4.17 (ddd, J = 54.7, 17.4, 5.5 Hz, 1H), 3.65 – 3.56 (m, 1H), 2.27 – 2.07 (m, 2H), 1.93 – 1.66 (m, 2H), 1.15 (dd, J = 6.4, 3.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 137.4, 131.9, 128.5, 128.0, 127.8, 127.6, 66.9, 52.5, 39.3, 34.1, 27.1, 19.3; (*major diastereoisomer*).

Spectral data are in accordance to the literature.[10]

4.7. 5-(5-((2,5-Dihydro-1*H*-pyrrol-1-yl)sulfonyl)-2-ethoxyphenyl)-1-methyl-3-propyl-1,6-dihydro-7*H*-pyrazolo[4,3-d]pyrimidin-7-one (8g)



The reaction was set up based on general procedure in 0.5 mmol scale using benzyl *N*,*N*-diallyl-4-ethoxy-3-(1-methyl-7-oxo-3-propyl-6,7-dihydro-1*H*-pyrazolo[4,3-d]pyrimidin-5-yl)benzenesulfonamide (**7g**) (241 mg, 0.5 mmol), **Ru-3^{C6}** complex (16.4 mg, 0.025 mmol) in toluene (5 mL) for 17 h at 80 °C. The product was purified by precipitation from toluene at −20 °C providing the desired product **8g** as a brownish solid (155 mg, 70% yield).

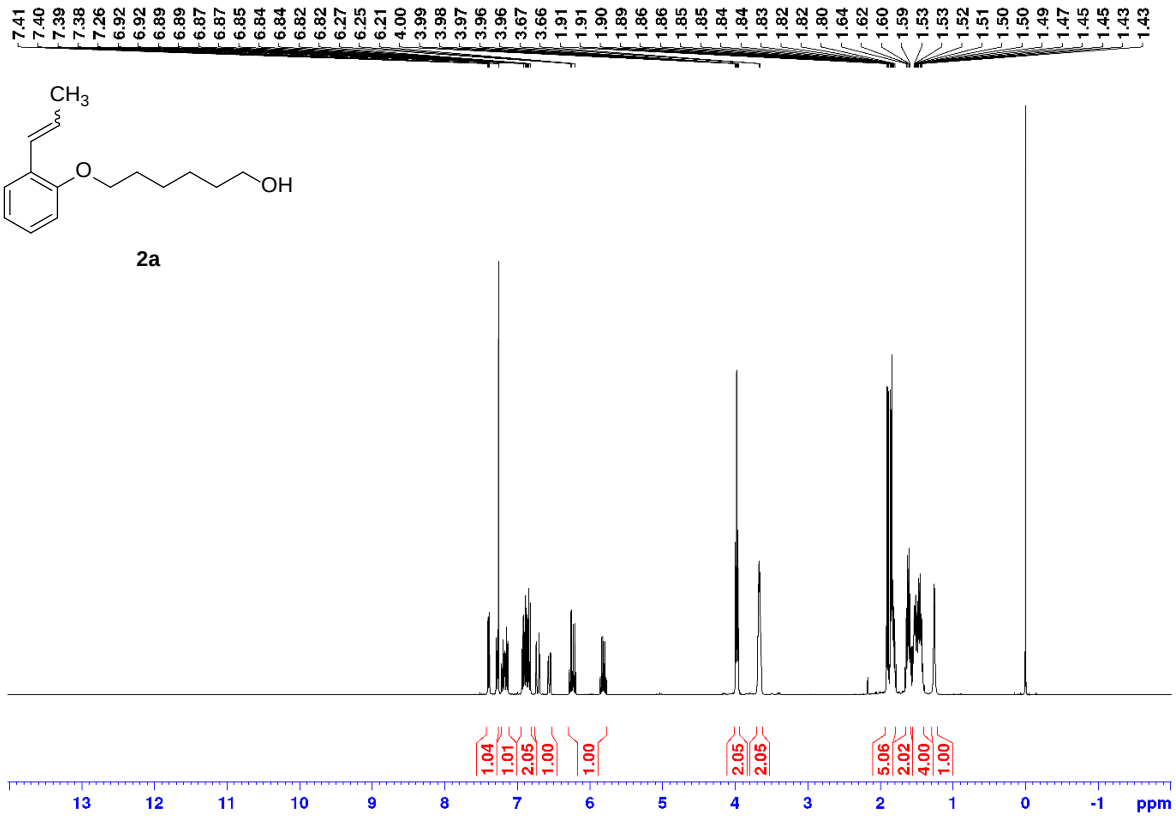
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.82 (s, 1H), 8.88 (d, J = 2.4 Hz, 1H), 7.91 (dd, J = 8.7, 2.4 Hz, 1H), 7.14 (d, J = 8.8 Hz, 1H), 5.69 (s, 2H), 4.36 (q, J = 6.9 Hz, 2H), 4.26 (s, 3H), 4.18 (s, 4H), 2.93 (t, J = 7.5 Hz, 2H), 1.91 − 1.80 (m, 2H), 1.63 (t, J = 7.0 Hz, 3H), 1.02 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 153.7, 147.1, 146.7, 138.5, 131.5, 131.1, 130.7, 125.6, 124.6, 121.3, 113.3, 66.2, 55.1, 38.4, 27.8, 22.4, 14.7, 14.2.

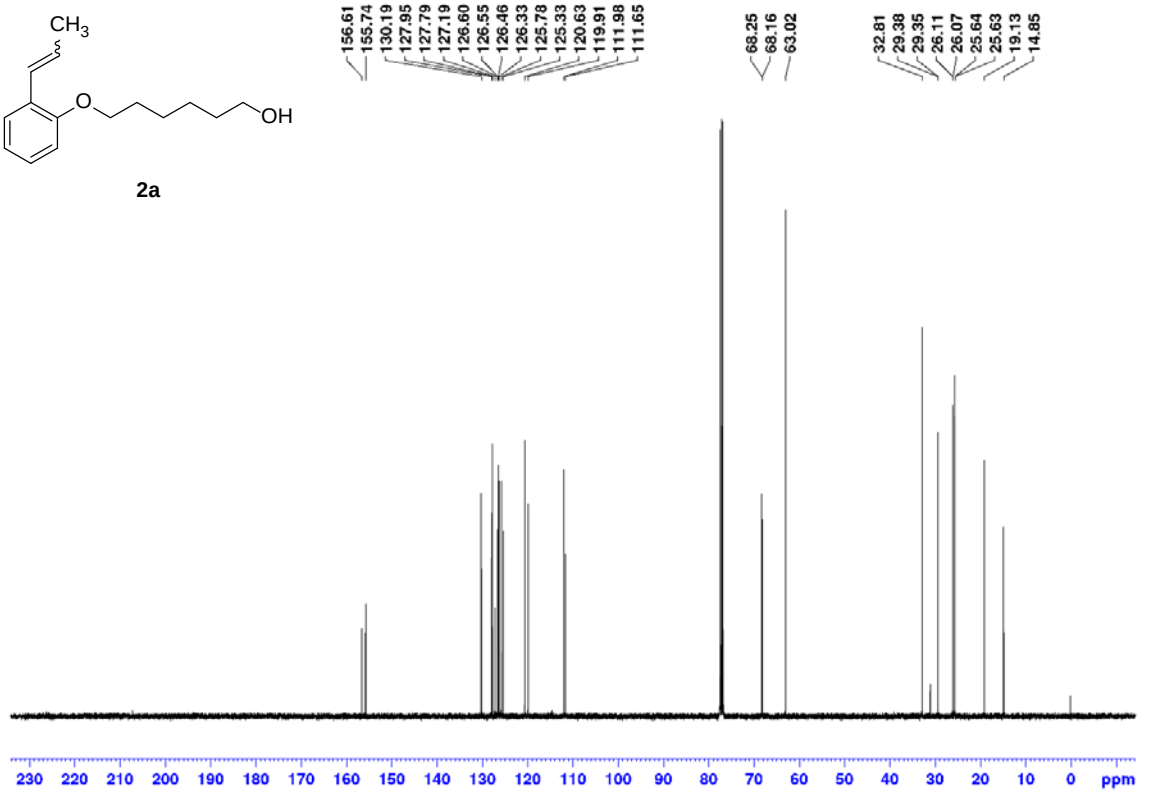
Spectral data are in accordance to the literature.[8]

5. NMR spectra of compounds

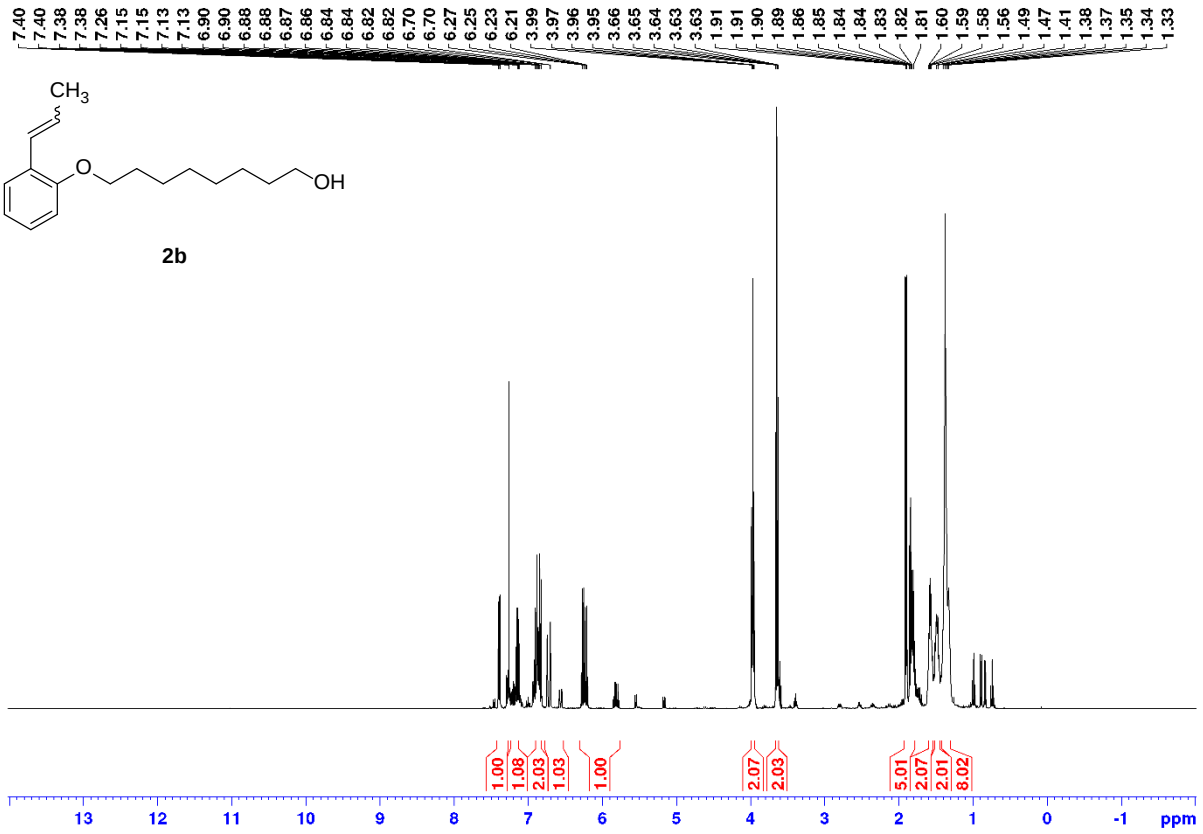
^{1}H NMR (400 MHz), $CDCl_3$



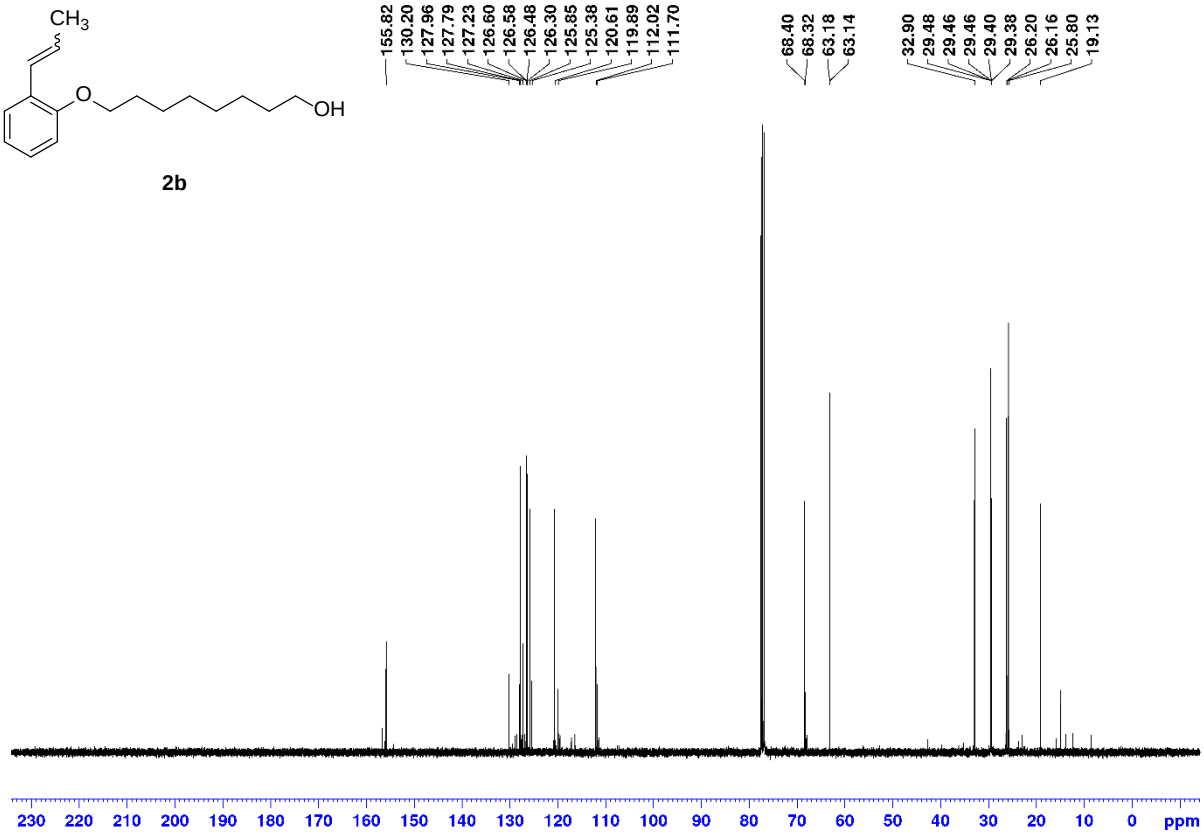
^{13}C NMR (101 MHz), $CDCl_3$



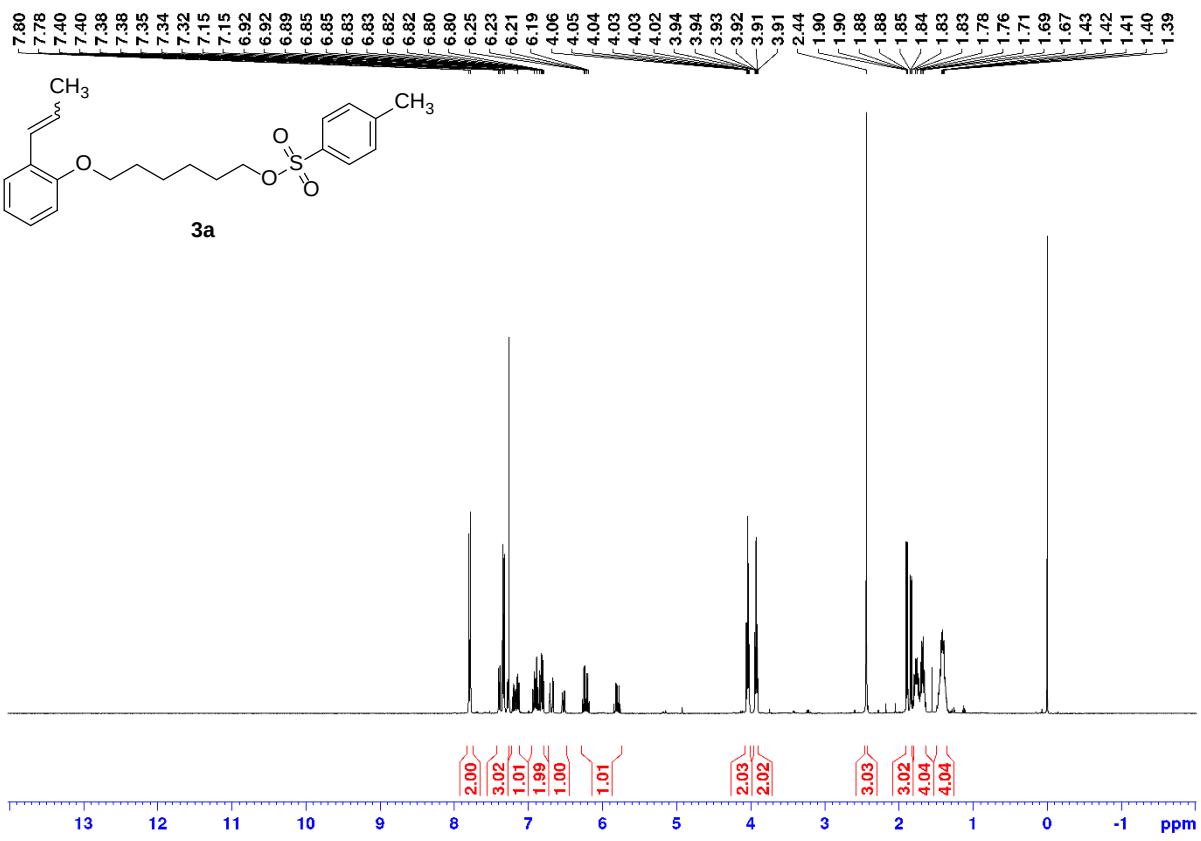
^{1}H NMR (400 MHz), $CDCl_3$



^{13}C NMR (101 MHz), $CDCl_3$

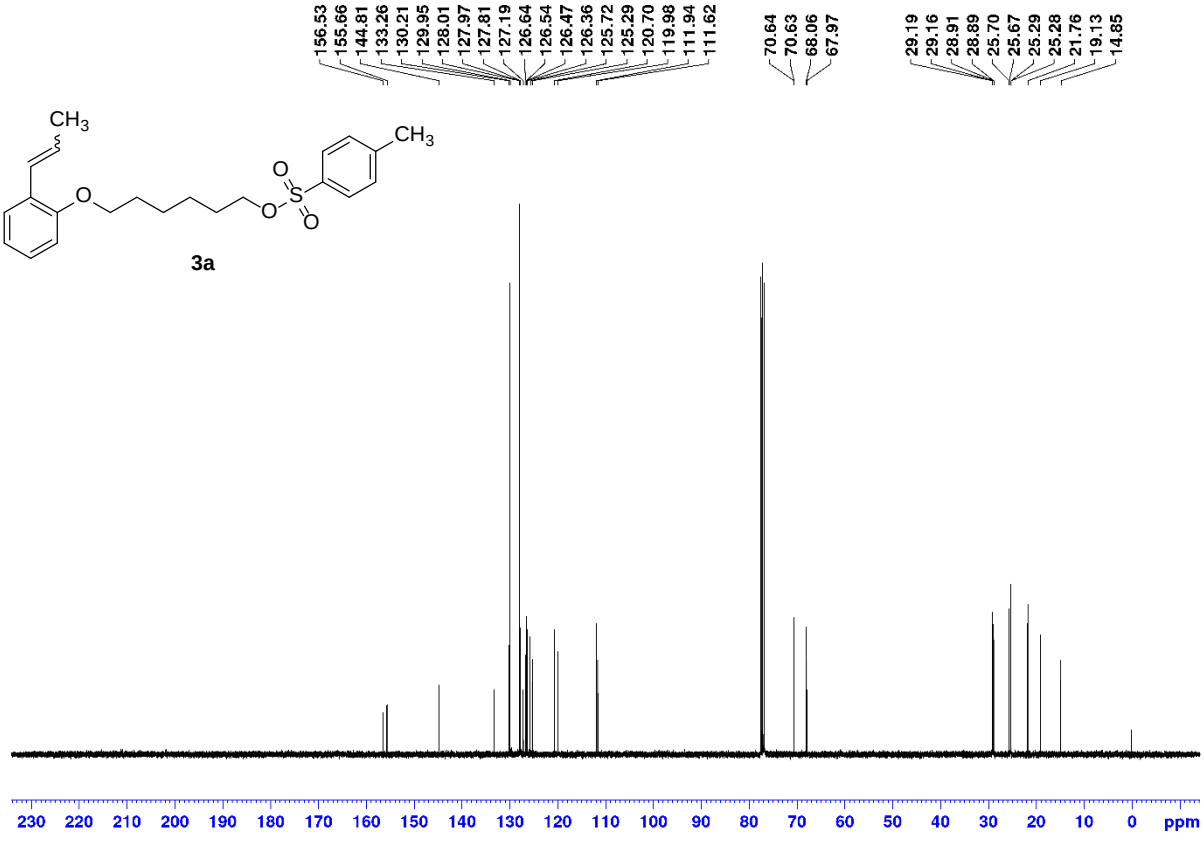


^{1}H NMR (400 MHz), $CDCl_3$



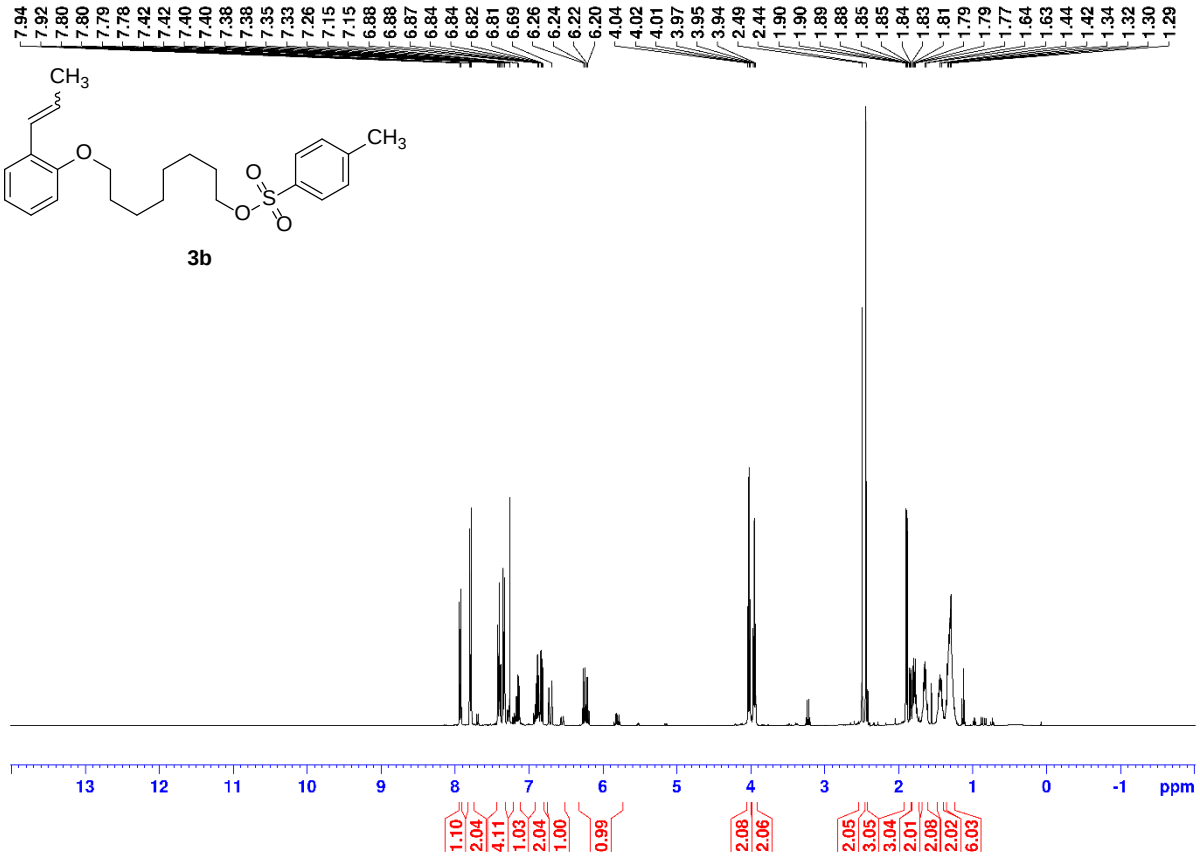
3a

^{13}C NMR (101 MHz), $CDCl_3$

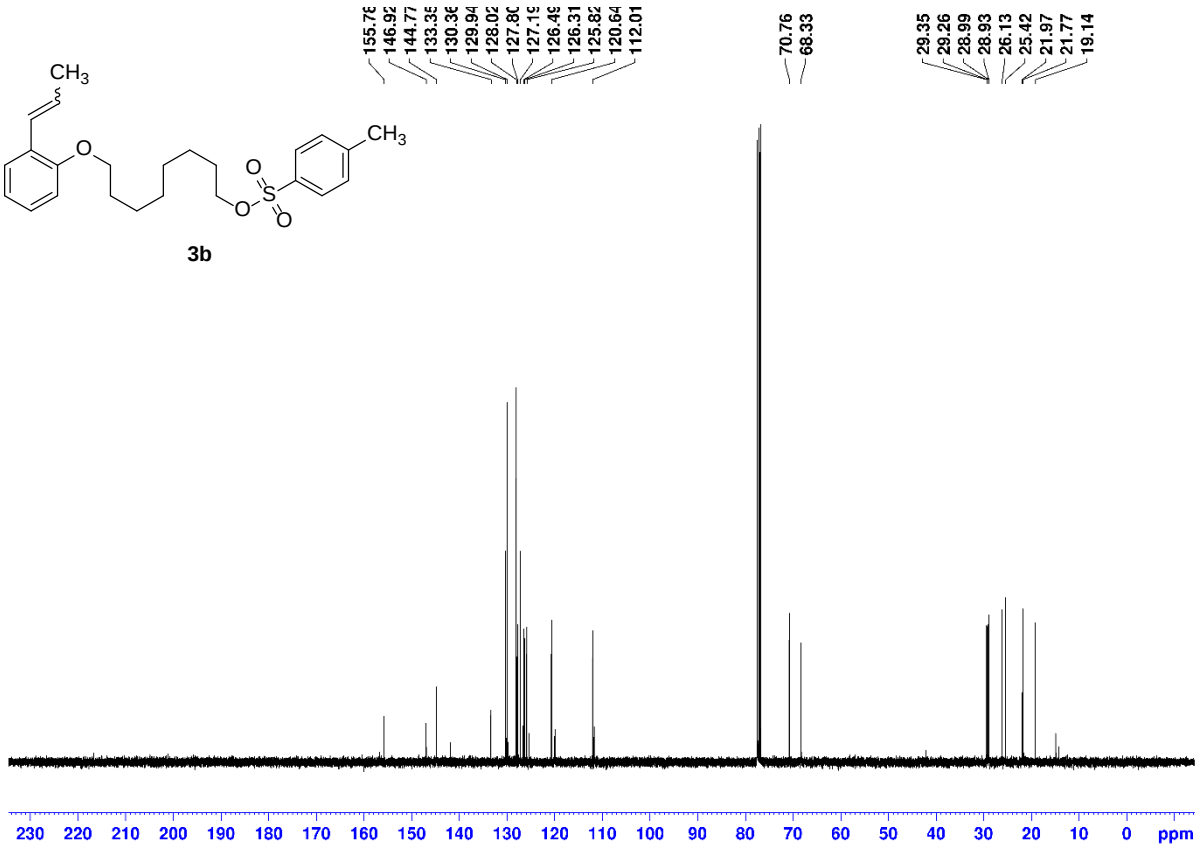


3a

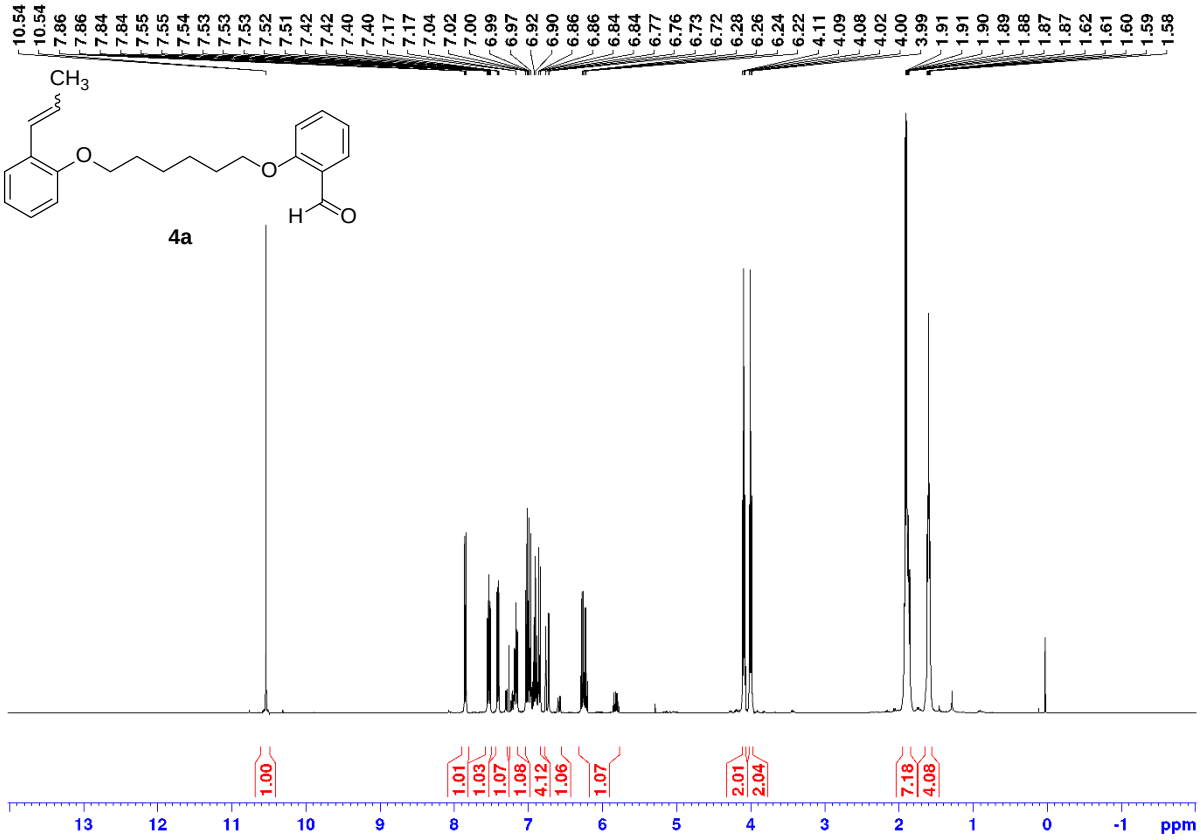
^{1}H NMR (400 MHz), $CDCl_3$



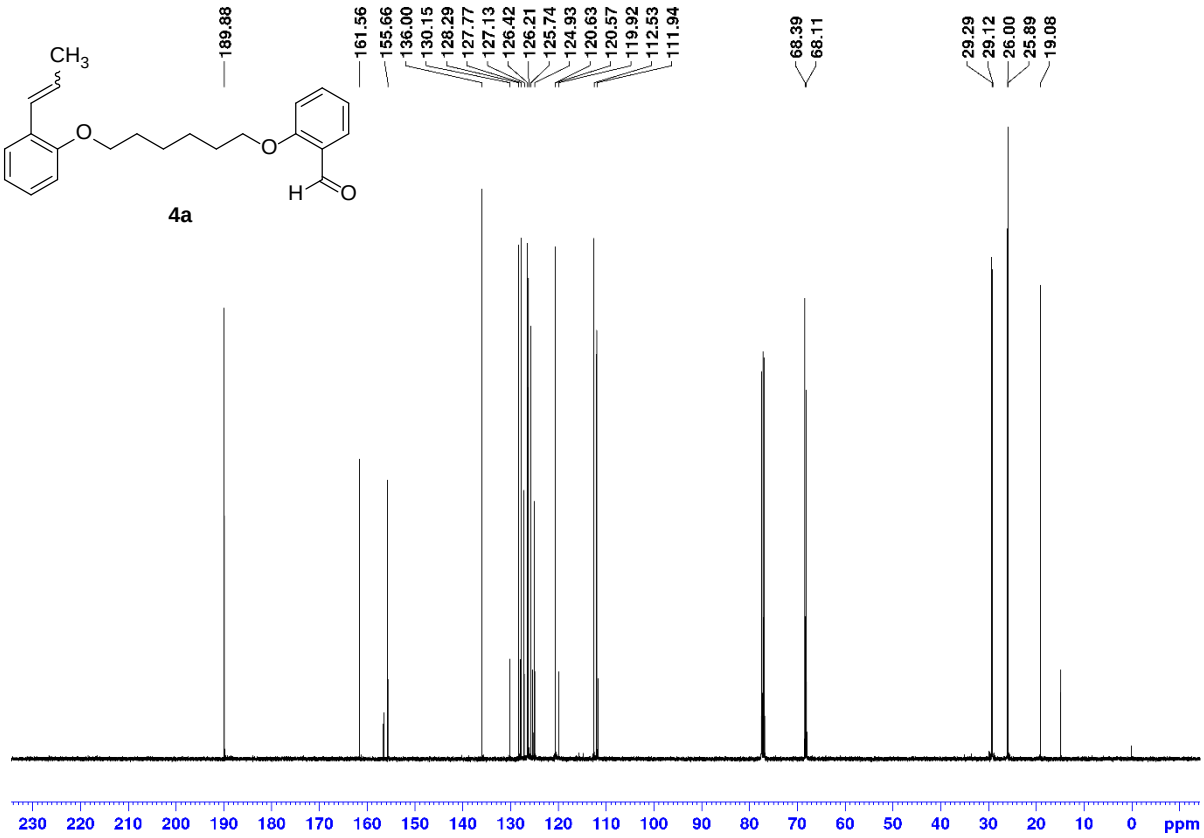
^{13}C NMR (101 MHz), $CDCl_3$



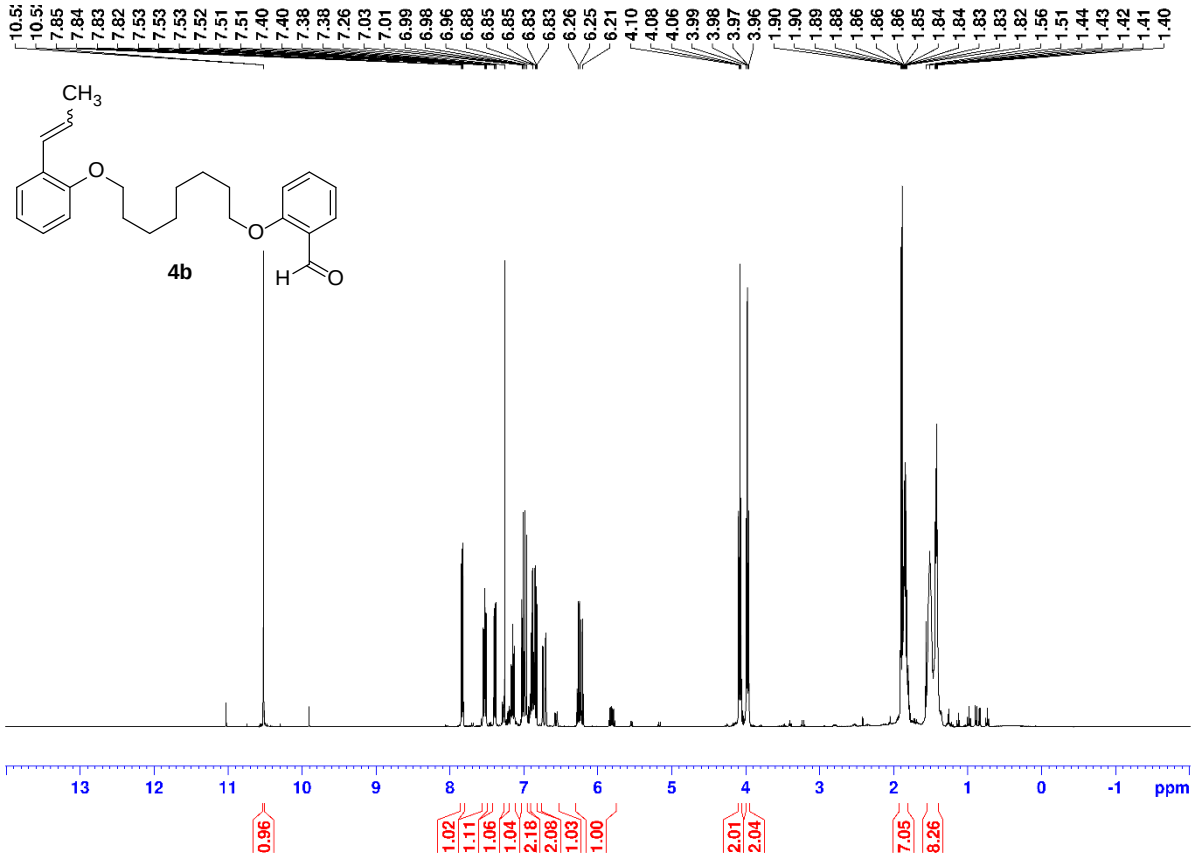
^{1}H NMR (400 MHz), $CDCl_3$



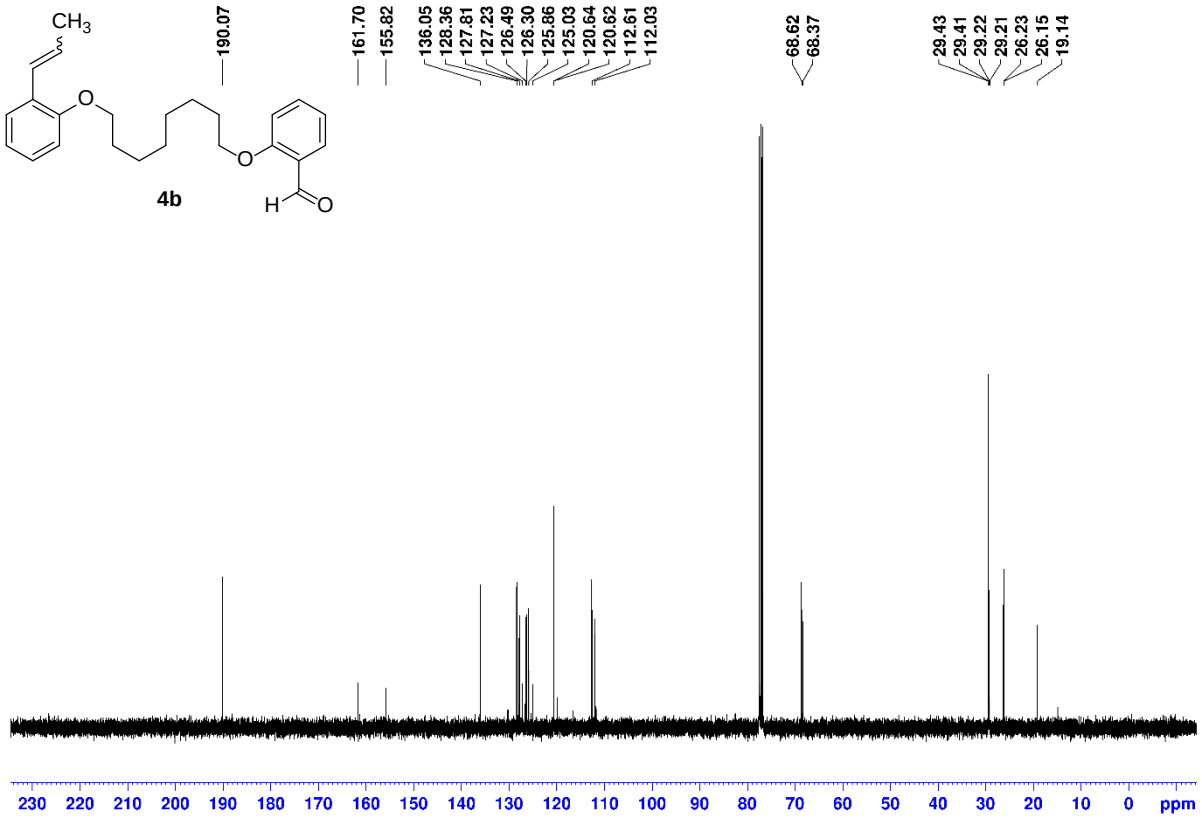
^{13}C NMR (101 MHz), $CDCl_3$



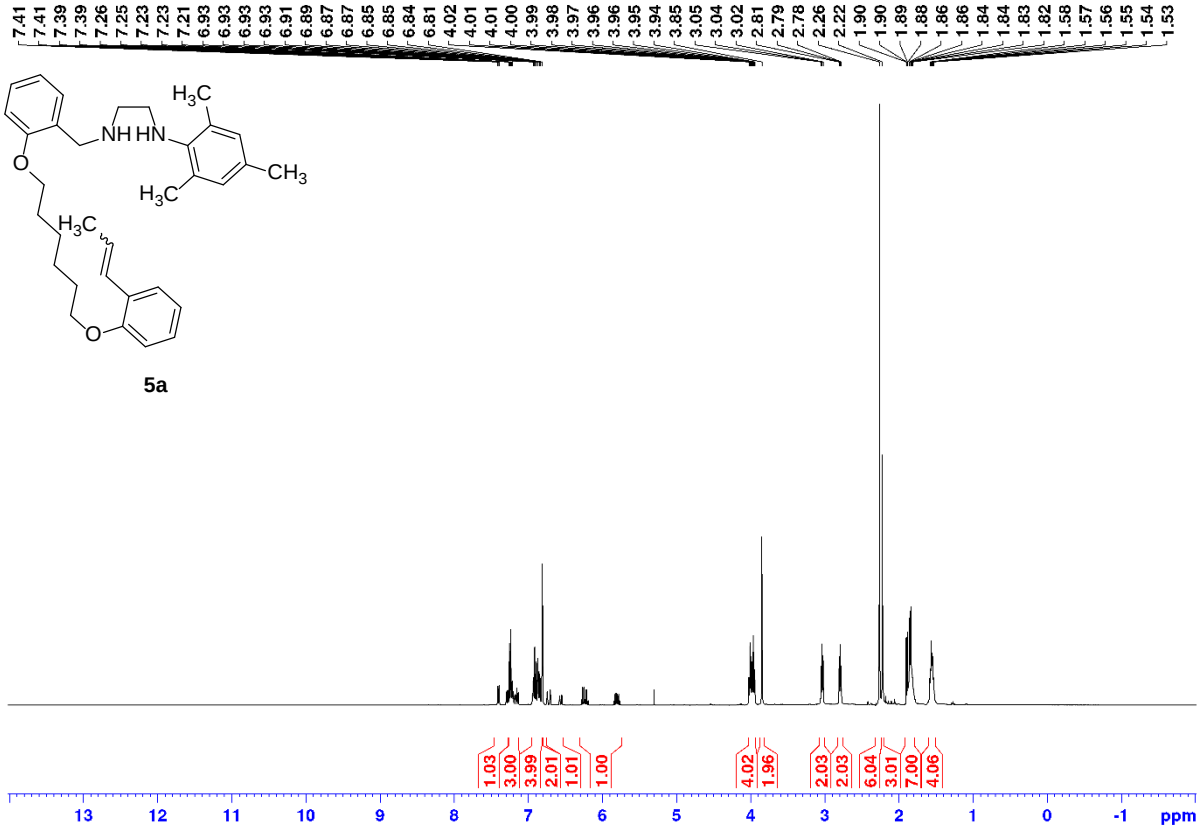
^{1}H NMR (400 MHz), $CDCl_3$



^{13}C NMR (101 MHz), $CDCl_3$

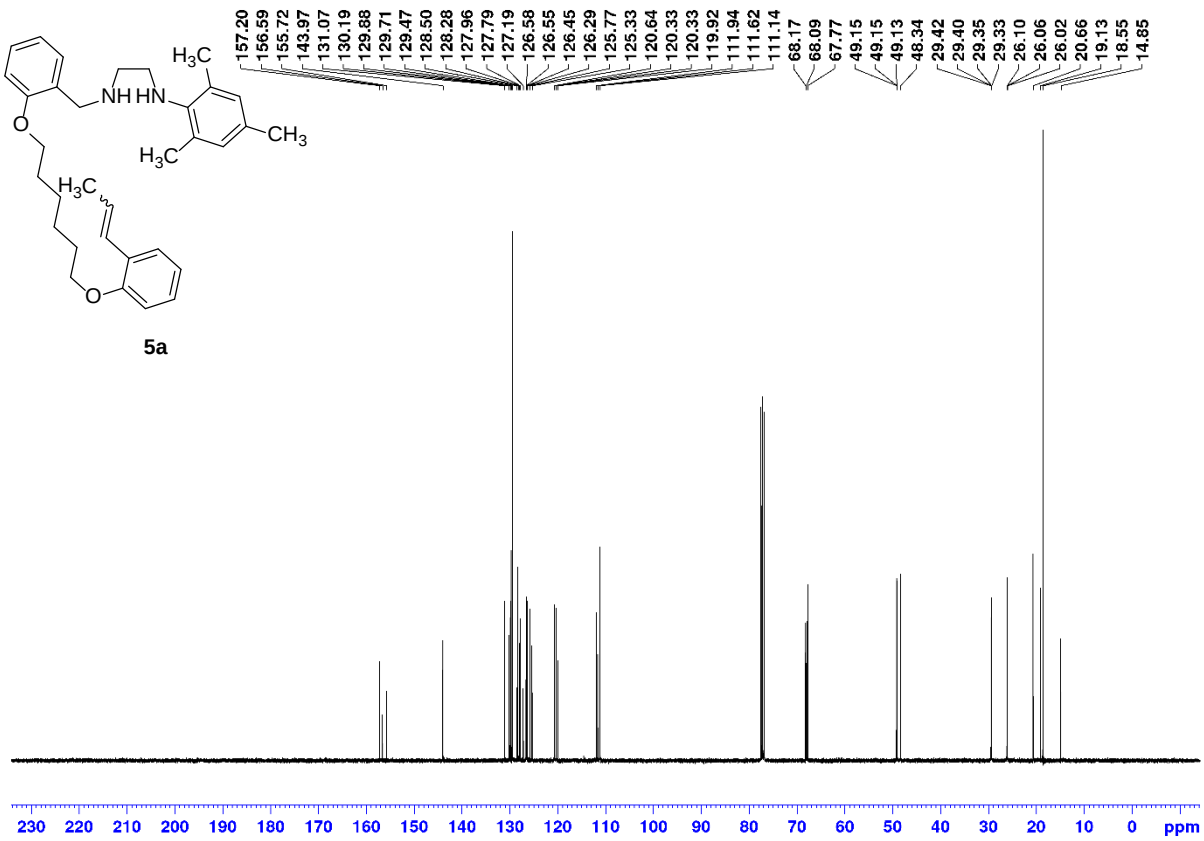


^{1}H NMR (400 MHz), $CDCl_3$



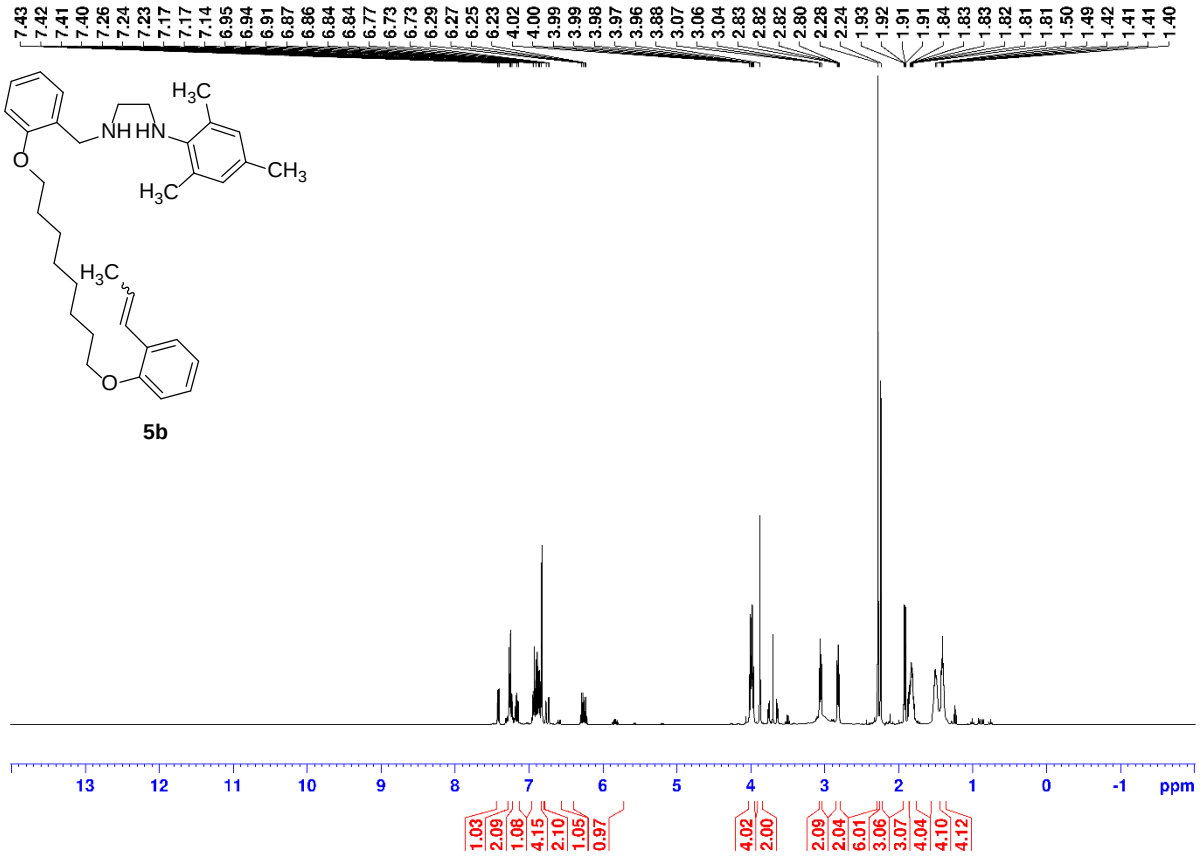
5a

^{13}C NMR (101 MHz), $CDCl_3$



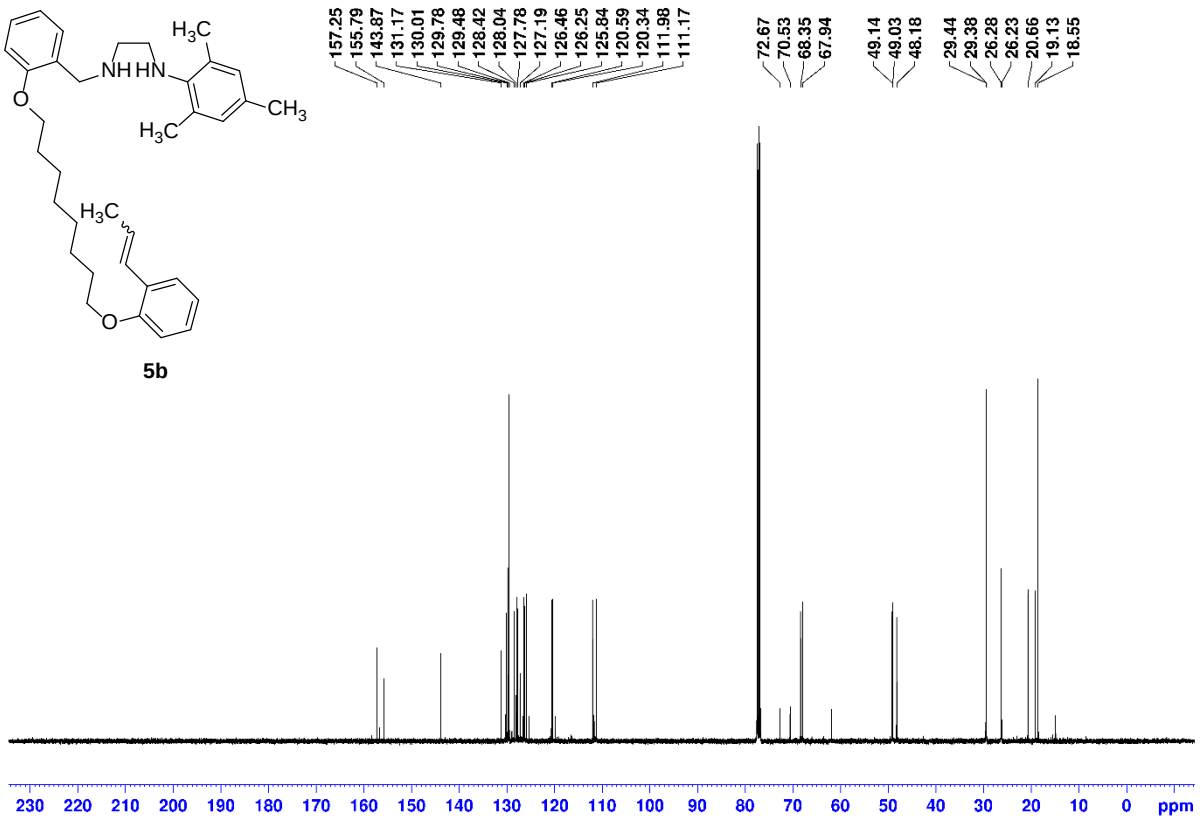
5a

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



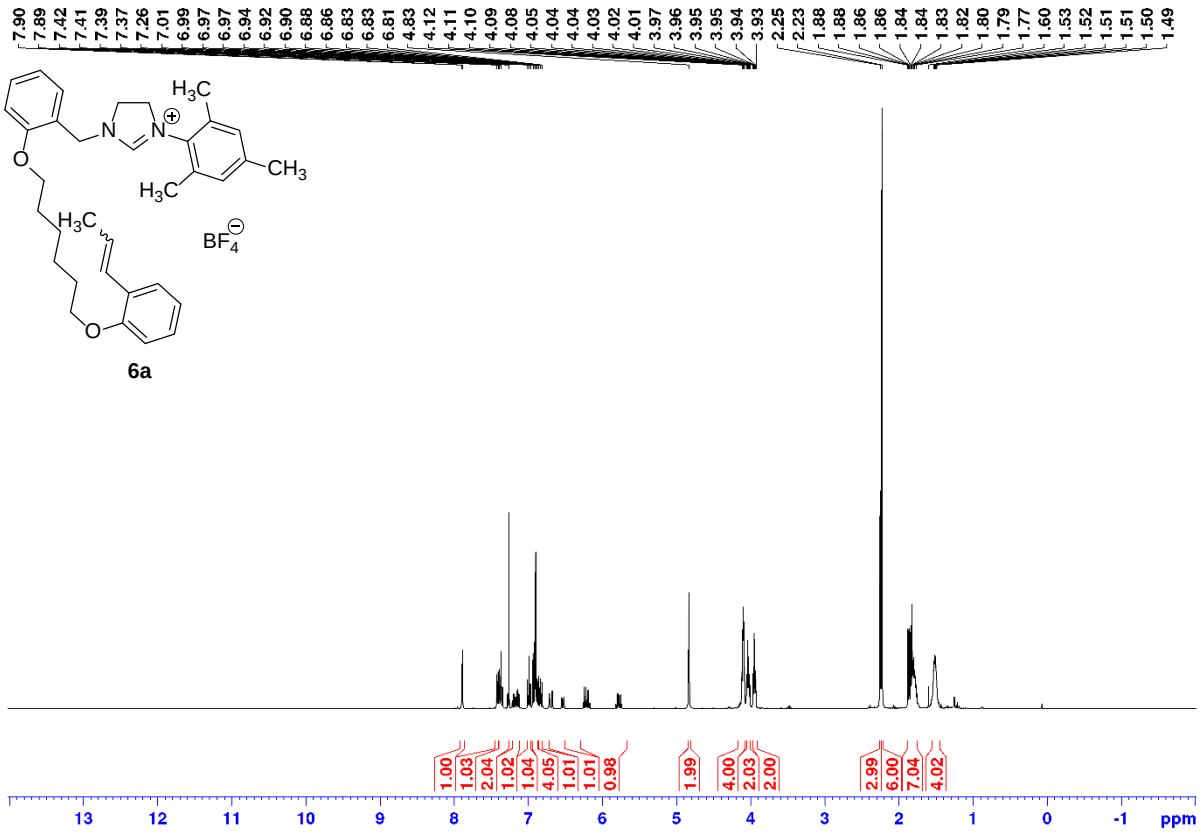
5b

^{13}C NMR (101 MHz), $CDCl_3$



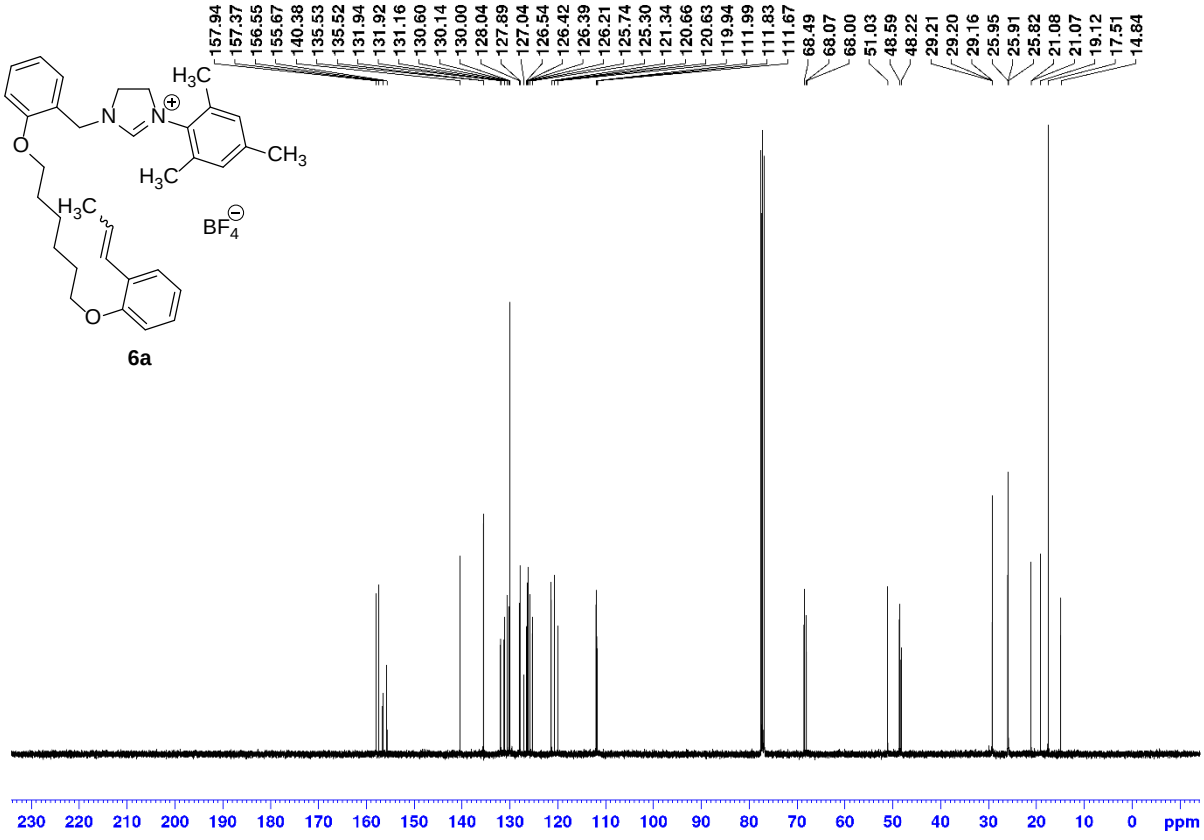
5b

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



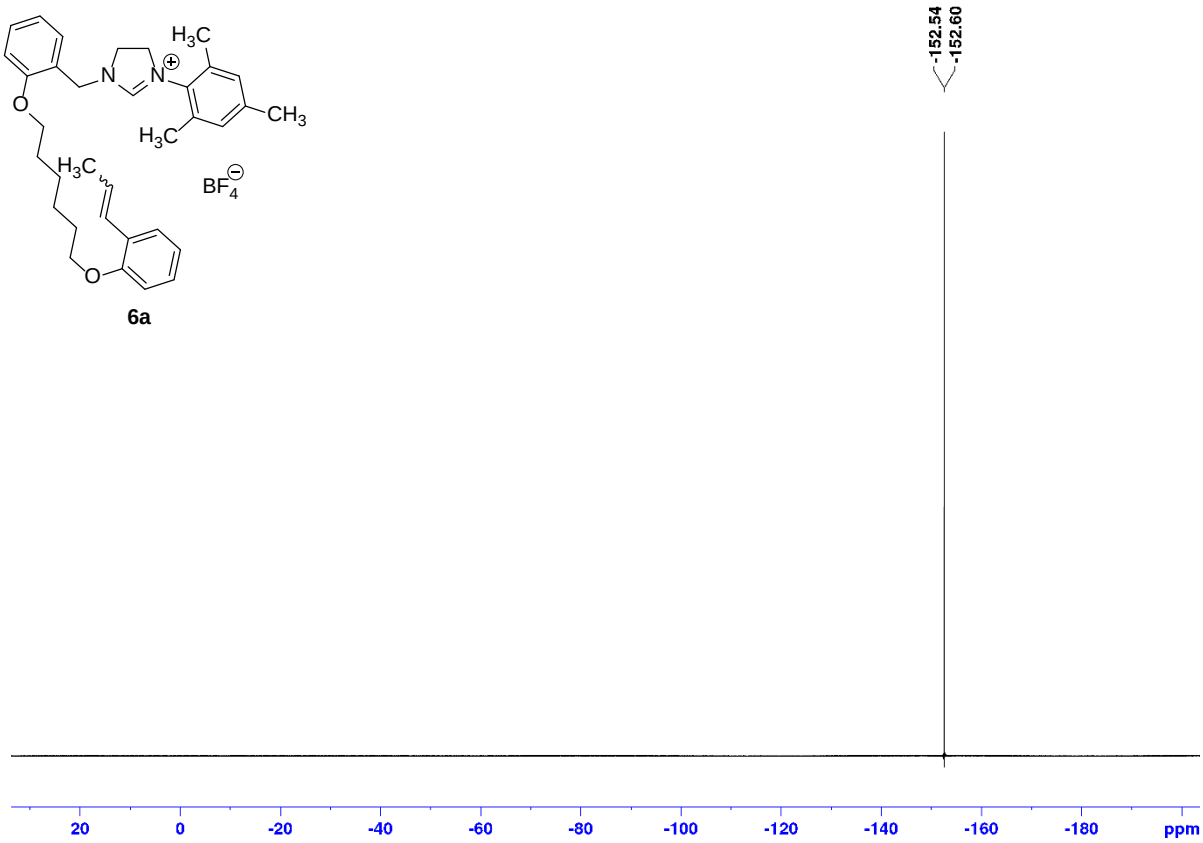
6a

^{13}C NMR (101 MHz), $CDCl_3$



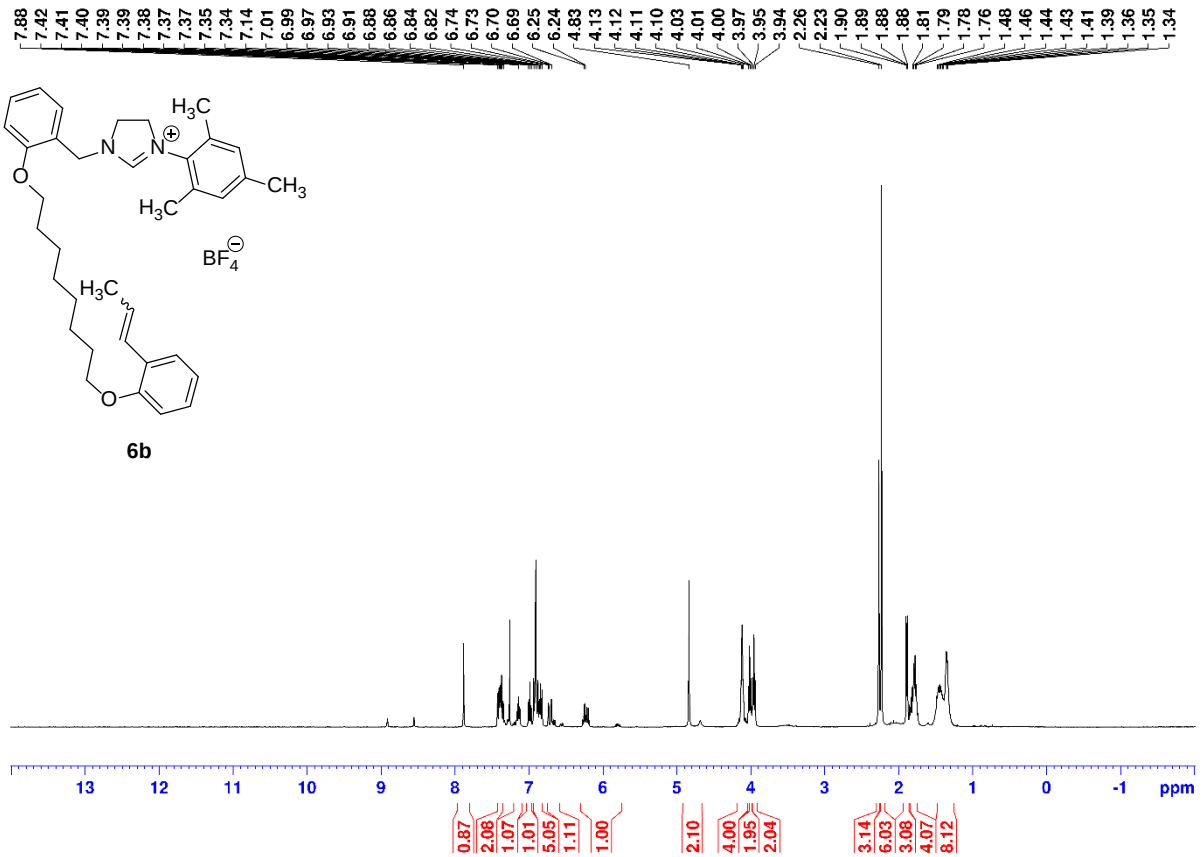
6a

^{19}F NMR (376 MHz), $CDCl_3$



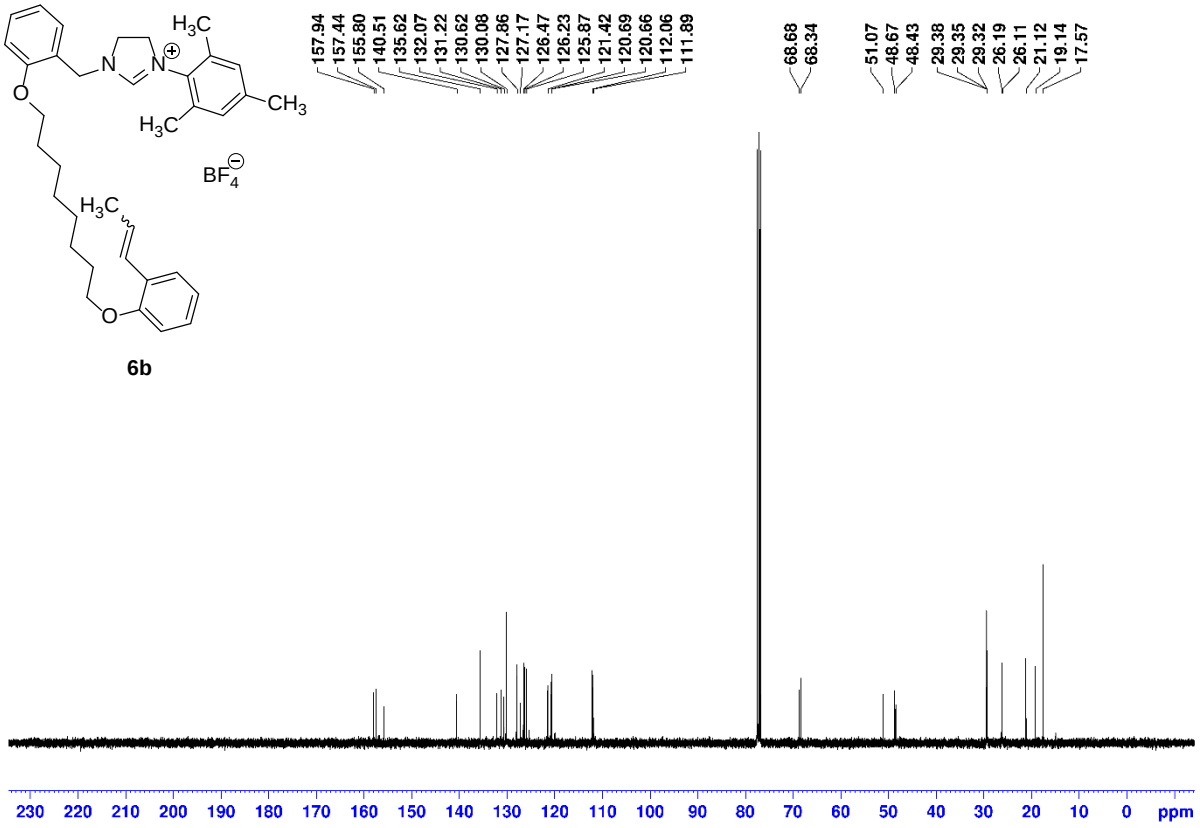
6a

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



6b

^{13}C NMR (101 MHz), $CDCl_3$

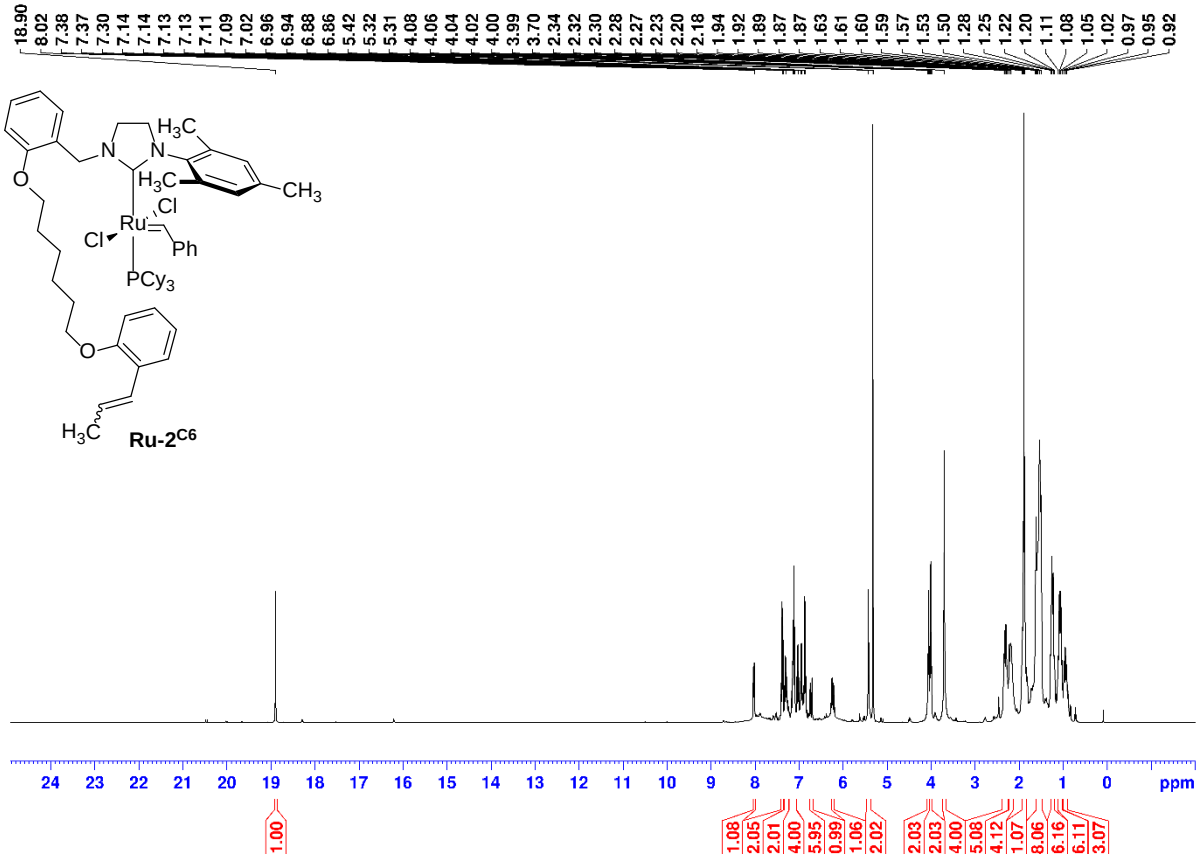


6b

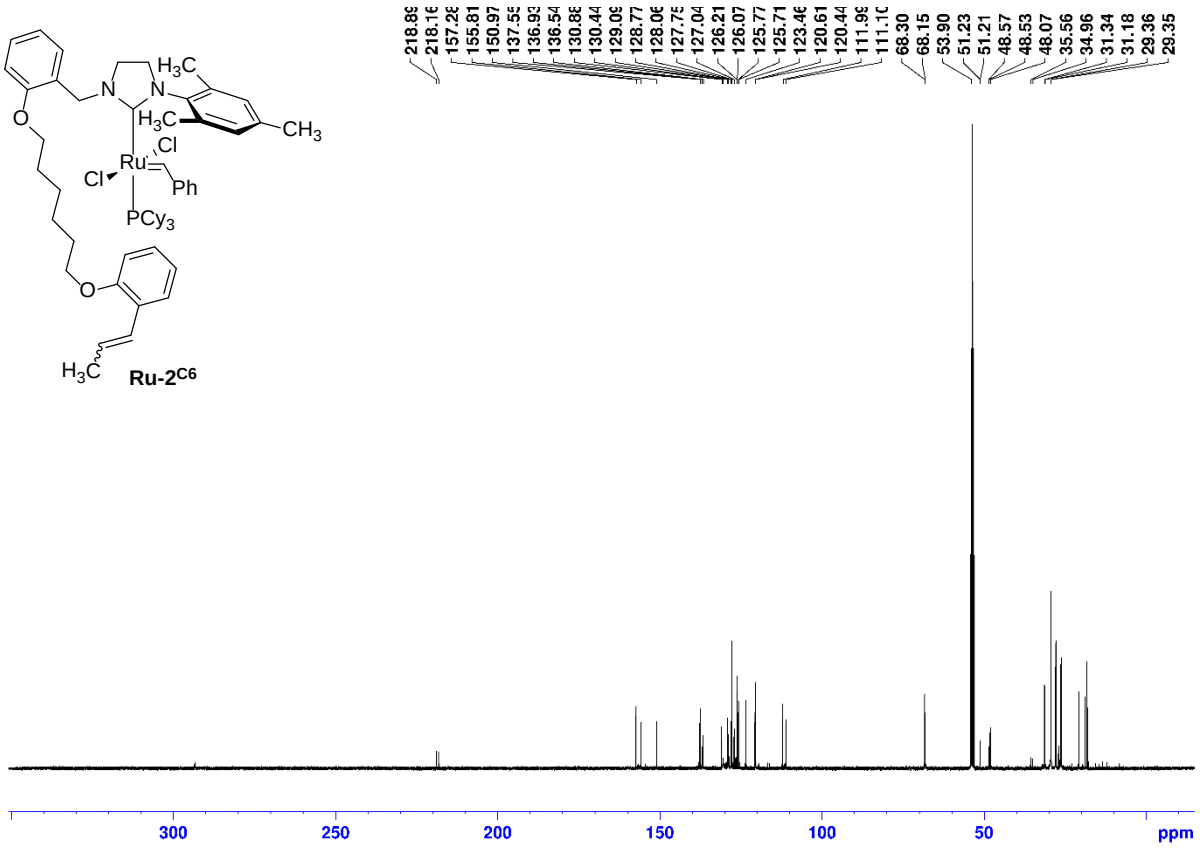
^{19}F NMR (376 MHz), $CDCl_3$

6b

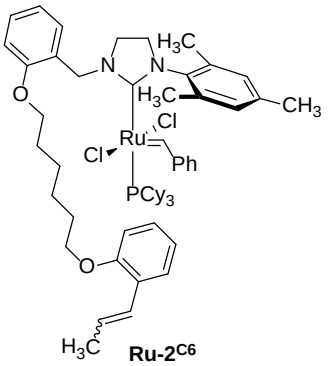
^{1}H NMR (400 MHz), CD_2Cl_2



^{13}C NMR (101 MHz), CD_2Cl_2

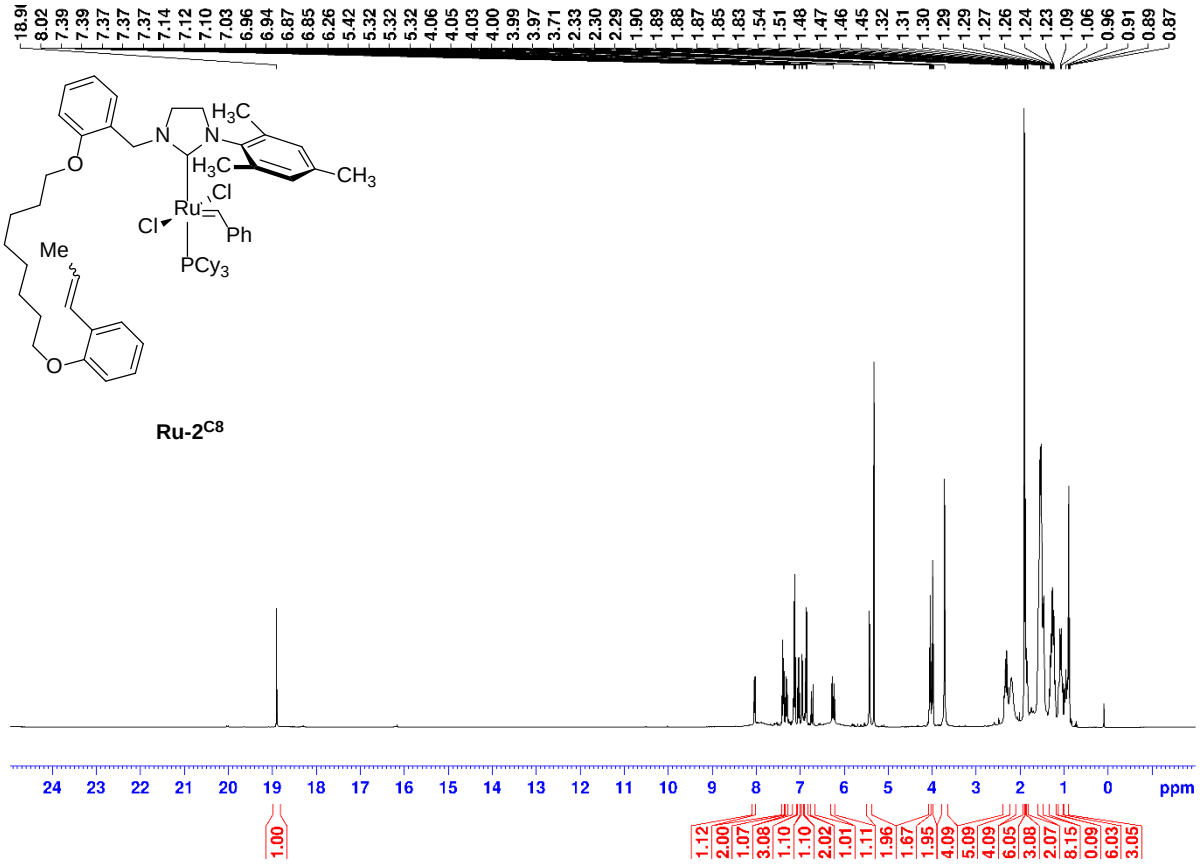


^{31}P NMR (162 MHz), CD_2Cl_2



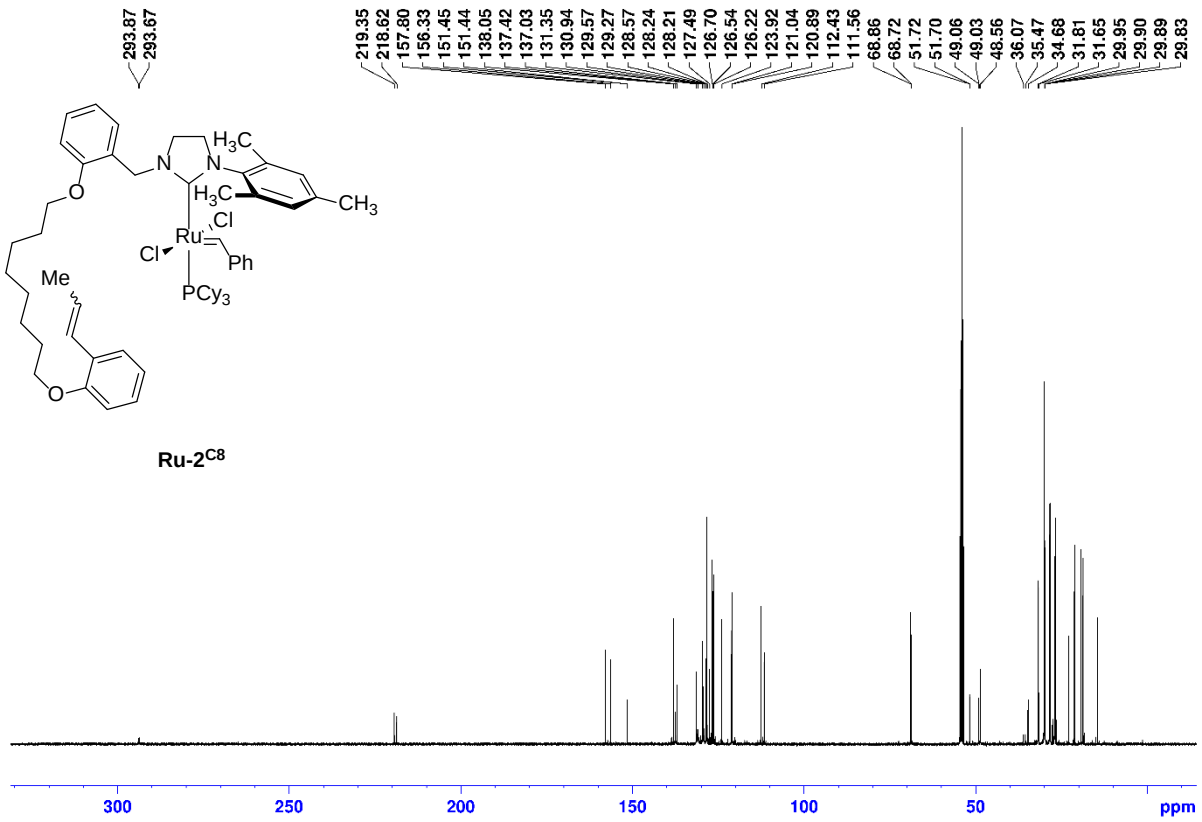
Ru-2^{C6}

^{1}H NMR (400 MHz), CD_2Cl_2



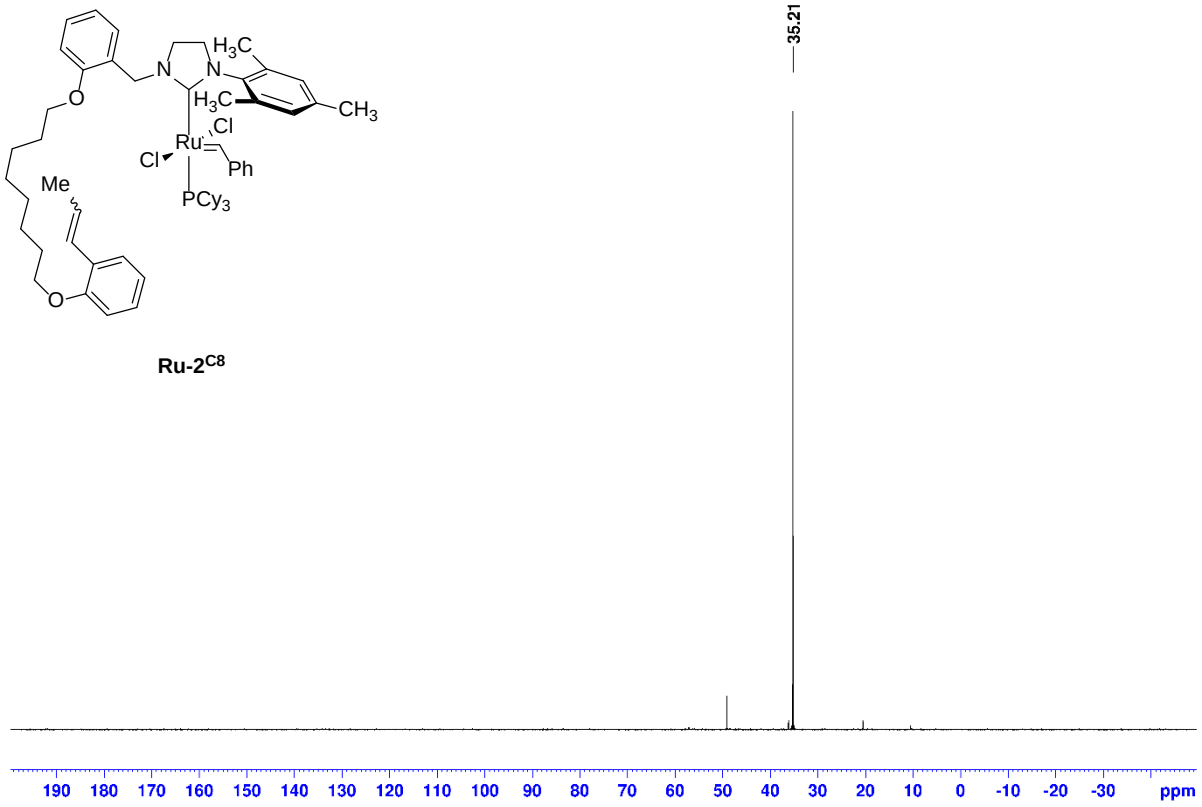
Ru-2^{C8}

^{13}C NMR (101 MHz), CD_2Cl_2



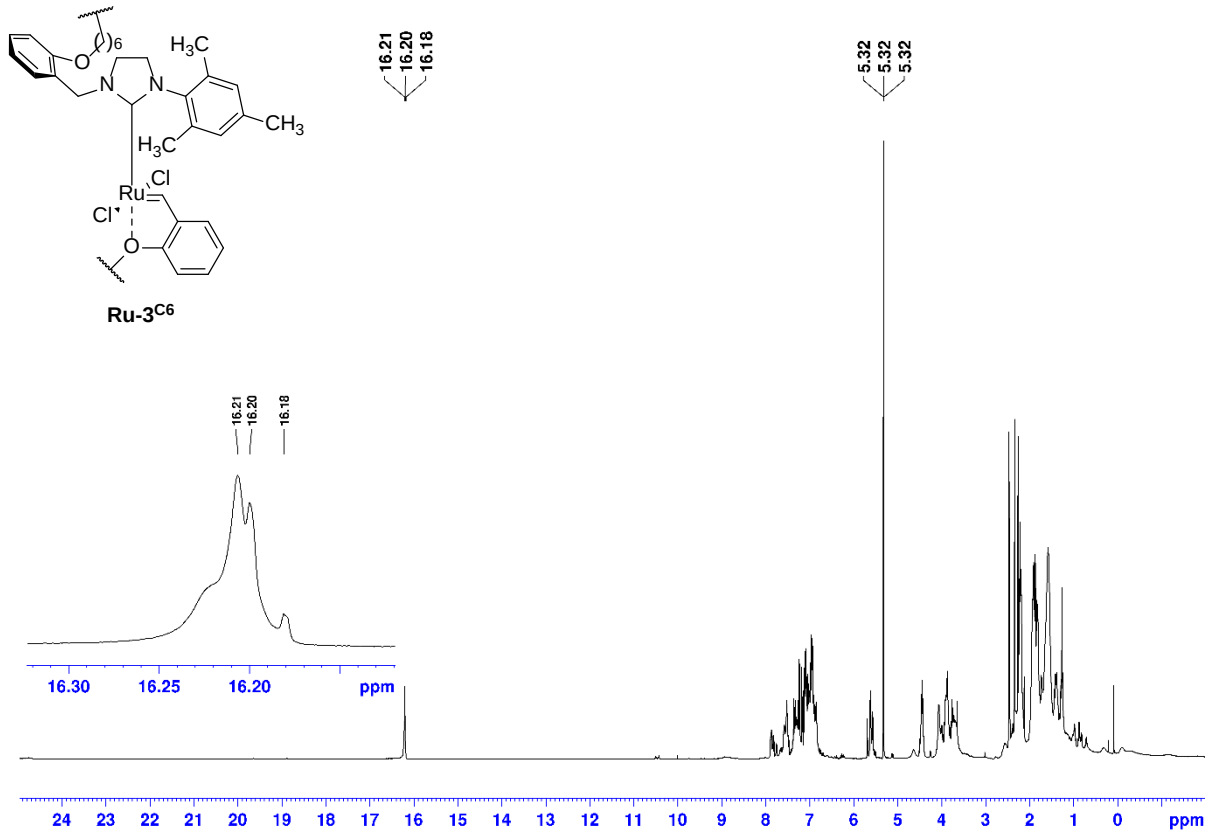
Ru-2^{C8}

^{31}P NMR (162 MHz), CD_2Cl_2

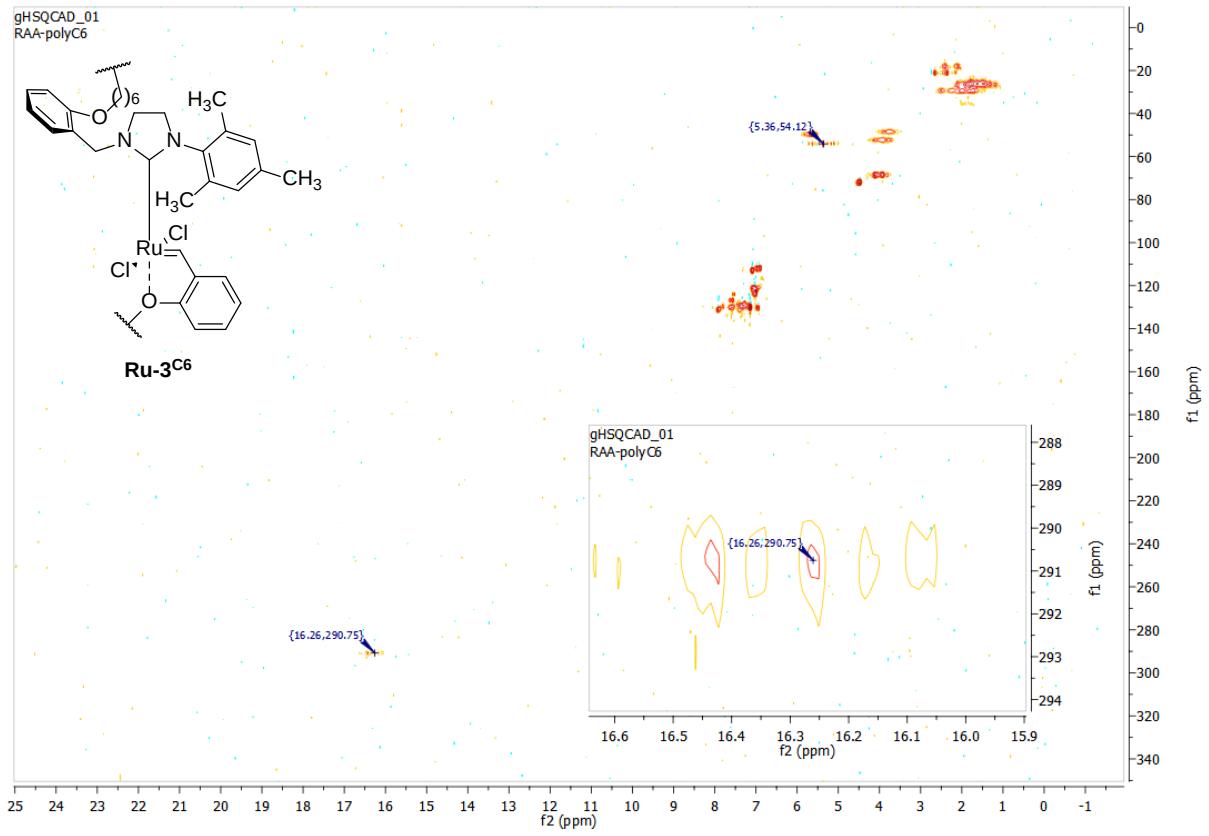


Ru-2^{C8}

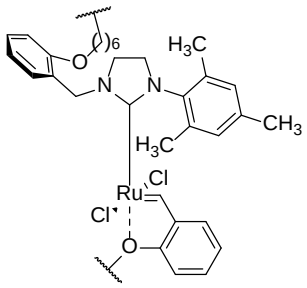
^{1}H NMR (400 MHz), CD_2Cl_2



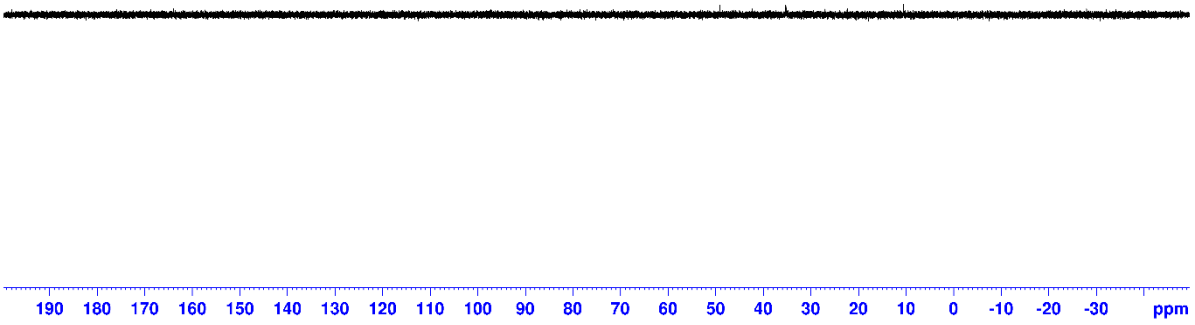
HSQC NMR (400 MHz), CD_2Cl_2



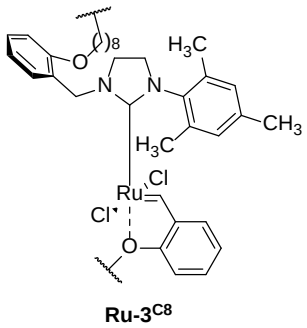
^{31}P NMR (162 MHz), CD_2Cl_2



Ru-3^{C6}

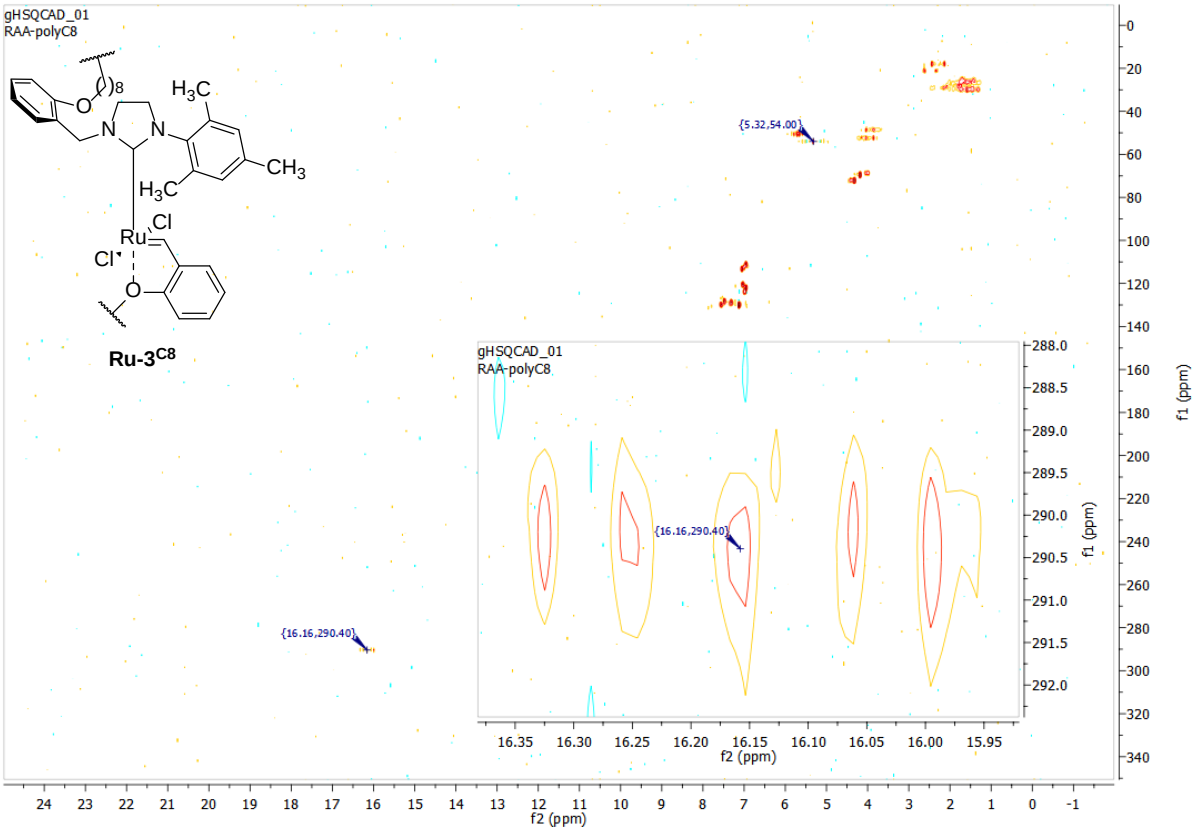


^{1}H NMR (400 MHz), CD_2Cl_2

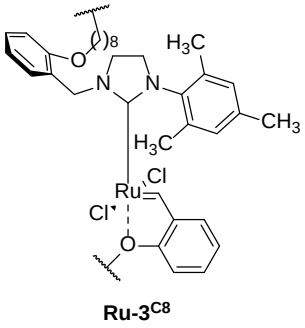


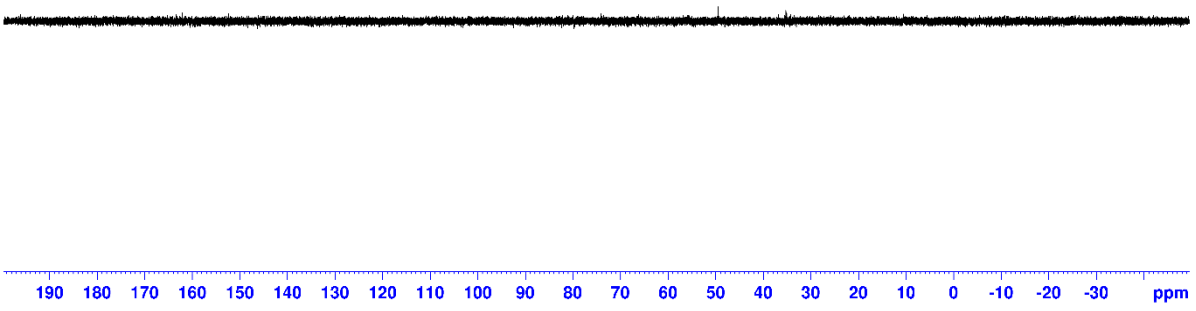
Ru-3^{C8}

HSQC NMR (400 MHz), CD_2Cl_2

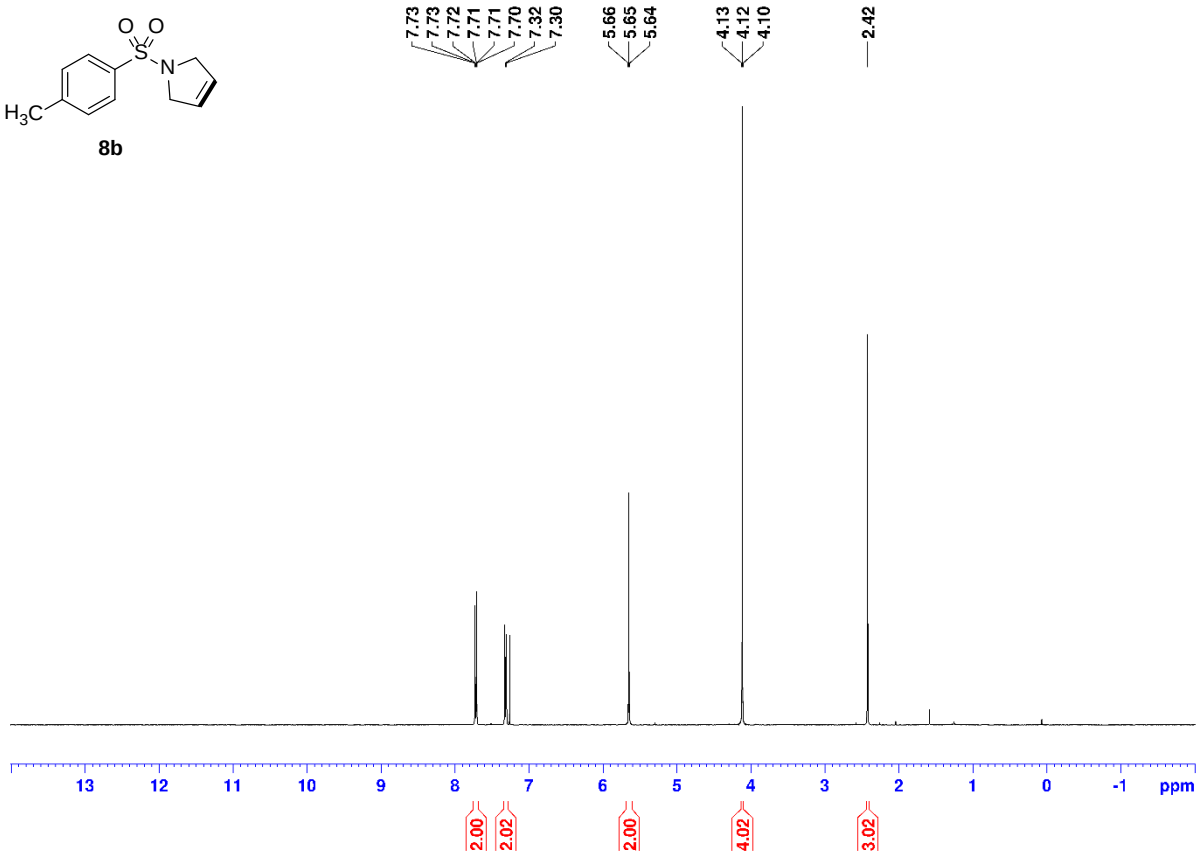


^{31}P NMR (162 MHz), CD_2Cl_2

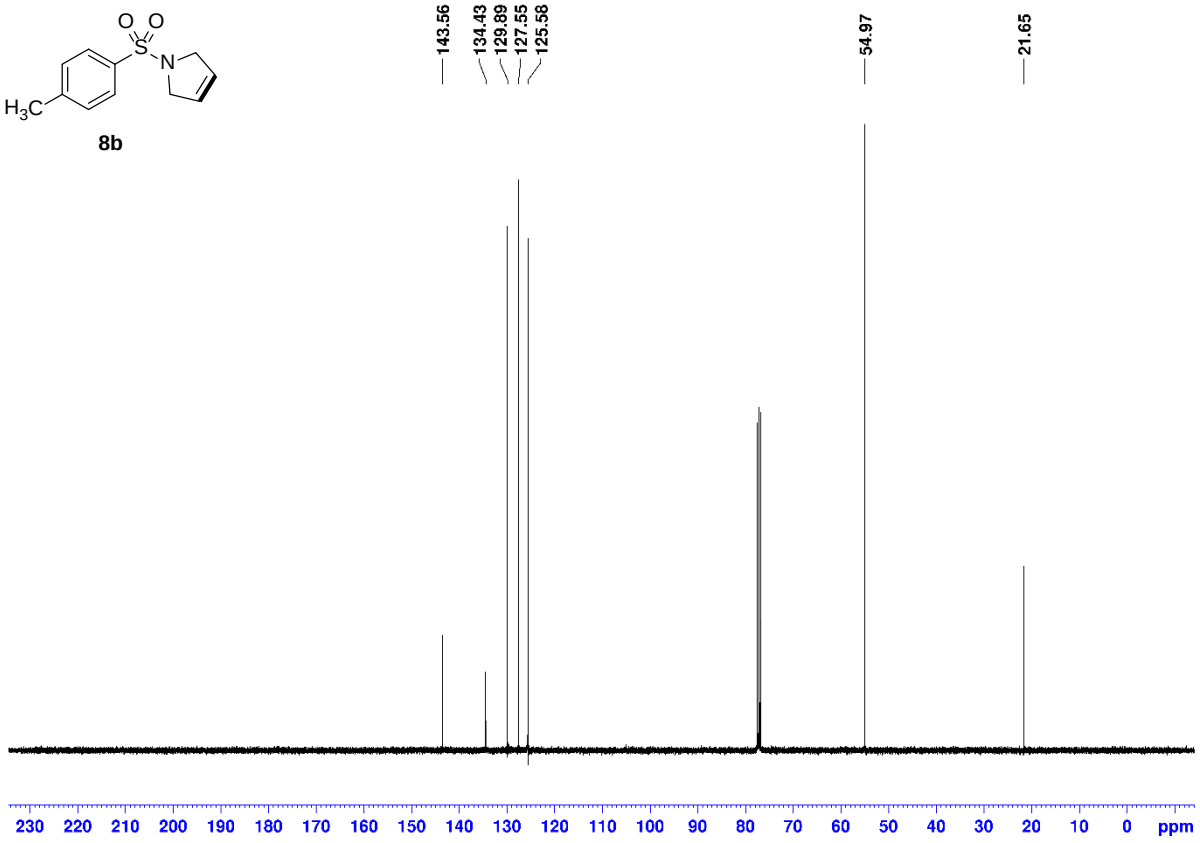




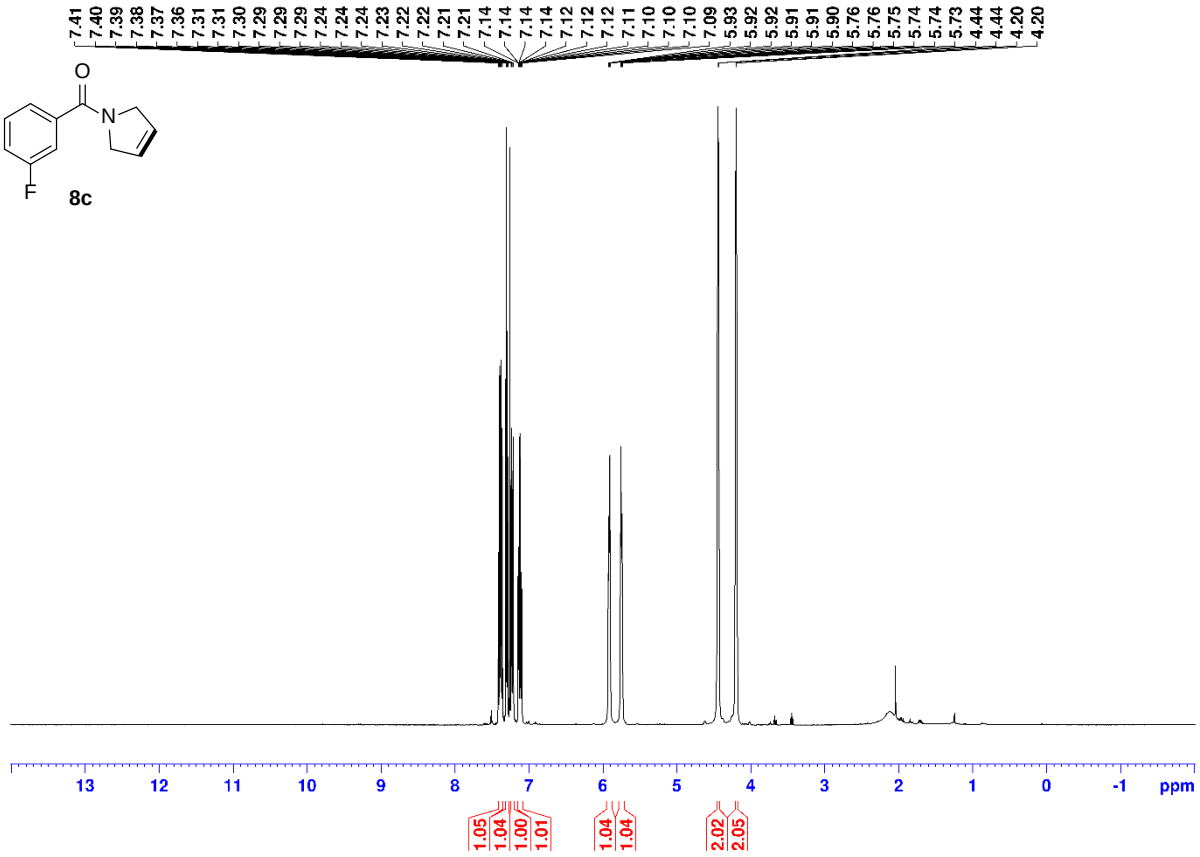
^{1}H NMR (400 MHz), $CDCl_3$



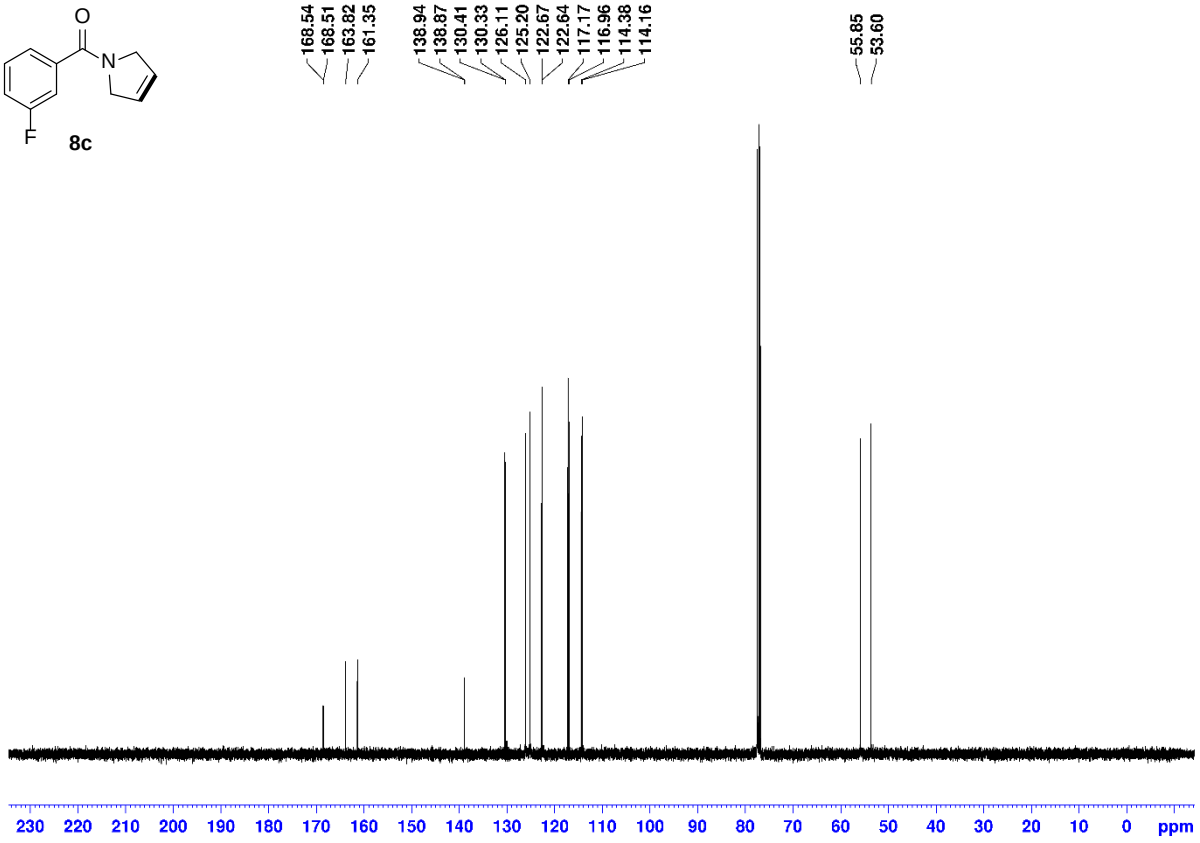
^{13}C NMR (101 MHz), $CDCl_3$



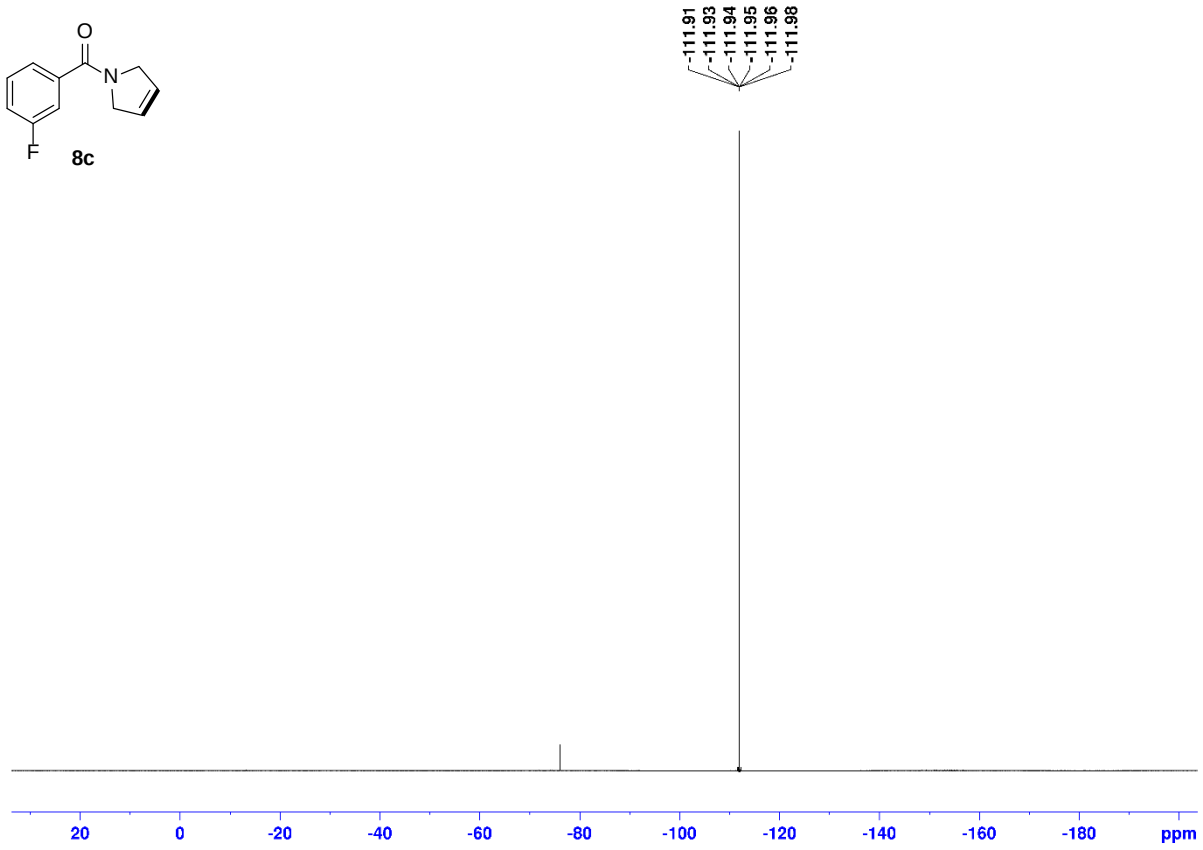
^{1}H NMR (400 MHz), $CDCl_3$



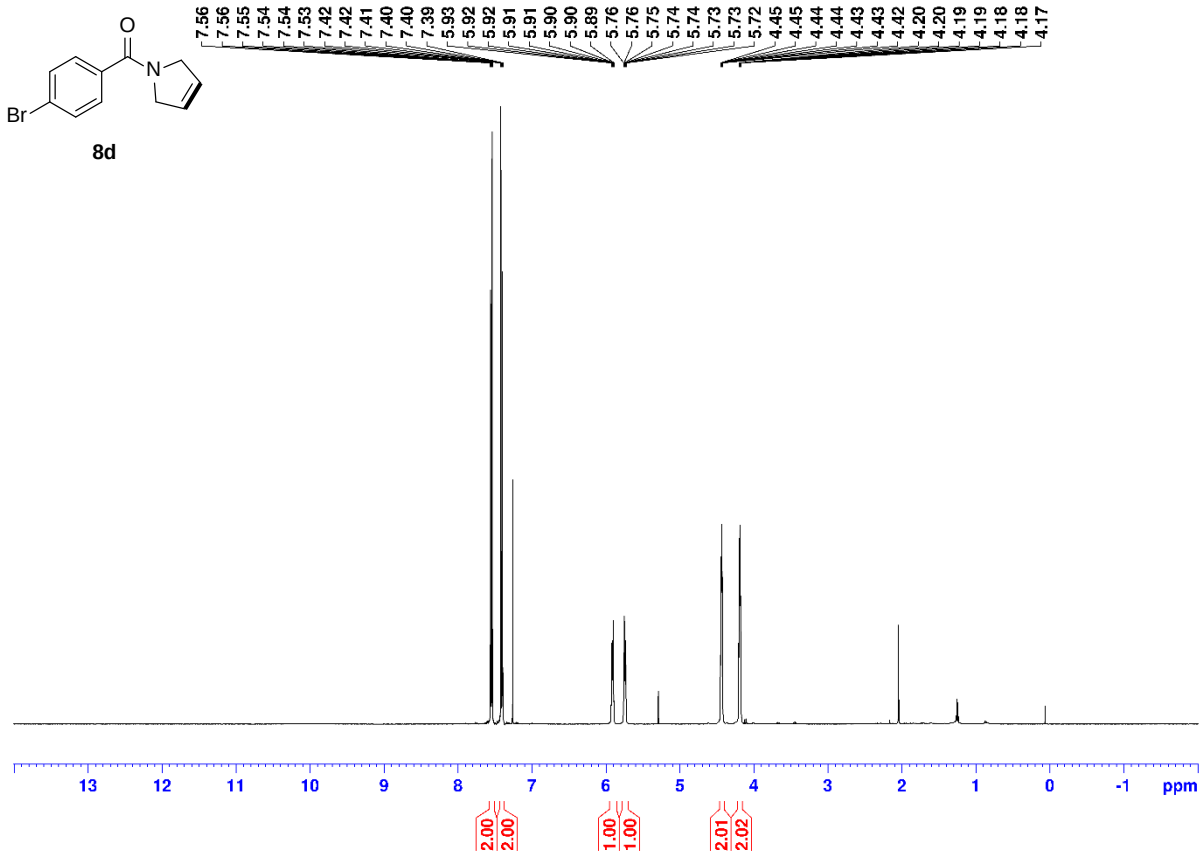
^{13}C NMR (101 MHz), $CDCl_3$



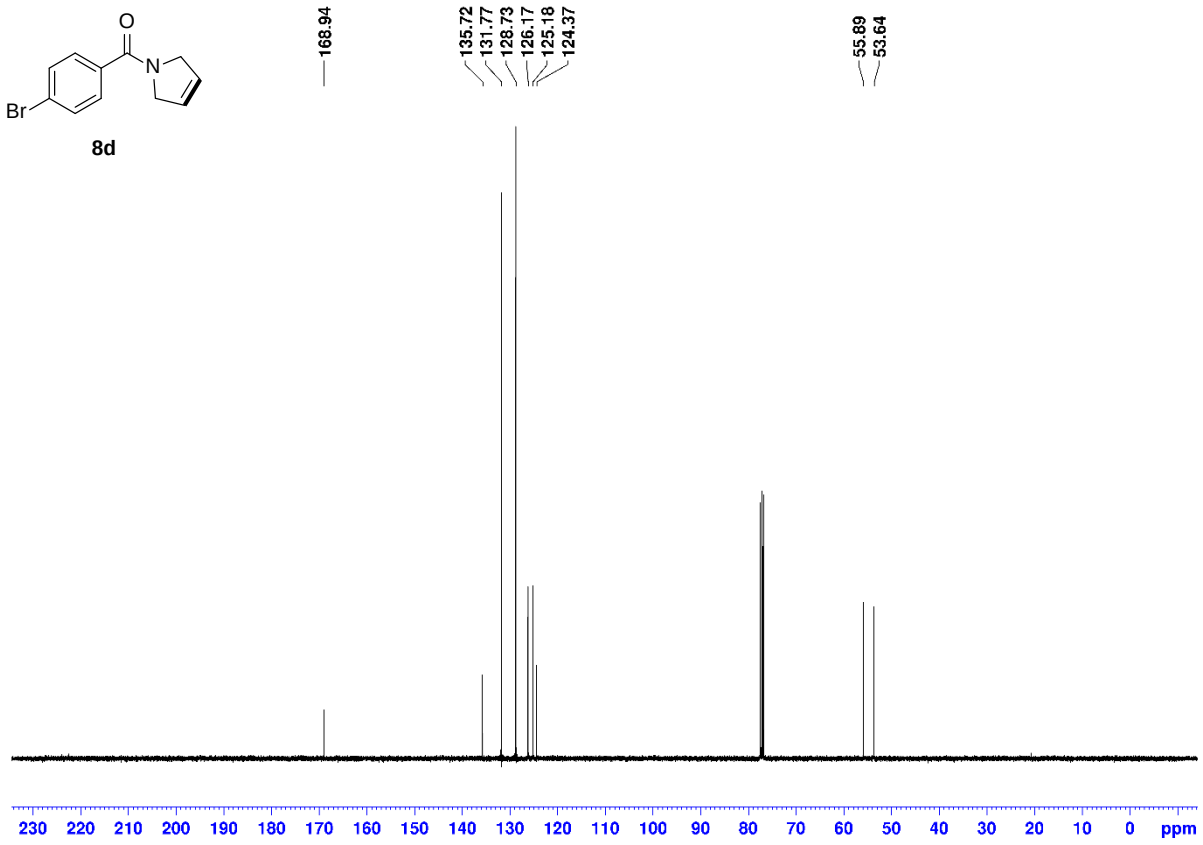
^{19}F NMR (376 MHz), $CDCl_3$



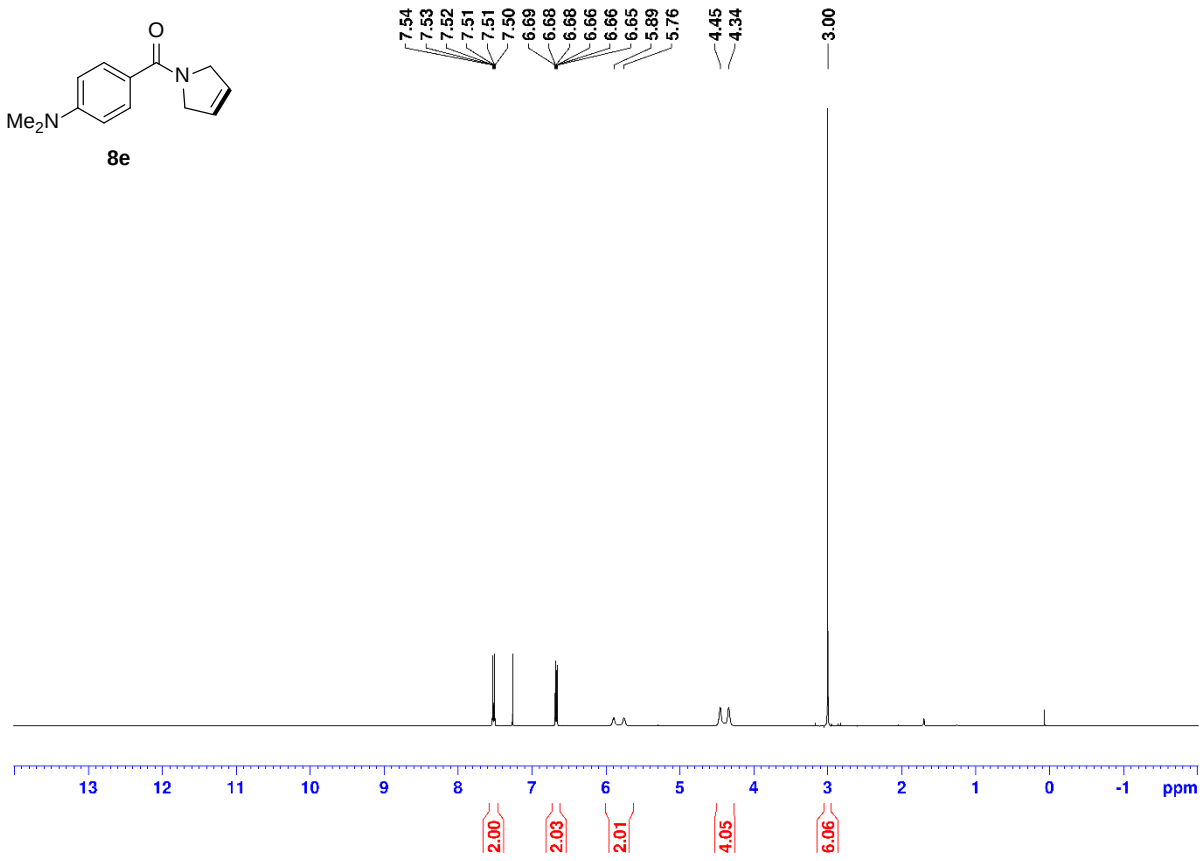
^{1}H NMR (400 MHz), $CDCl_3$



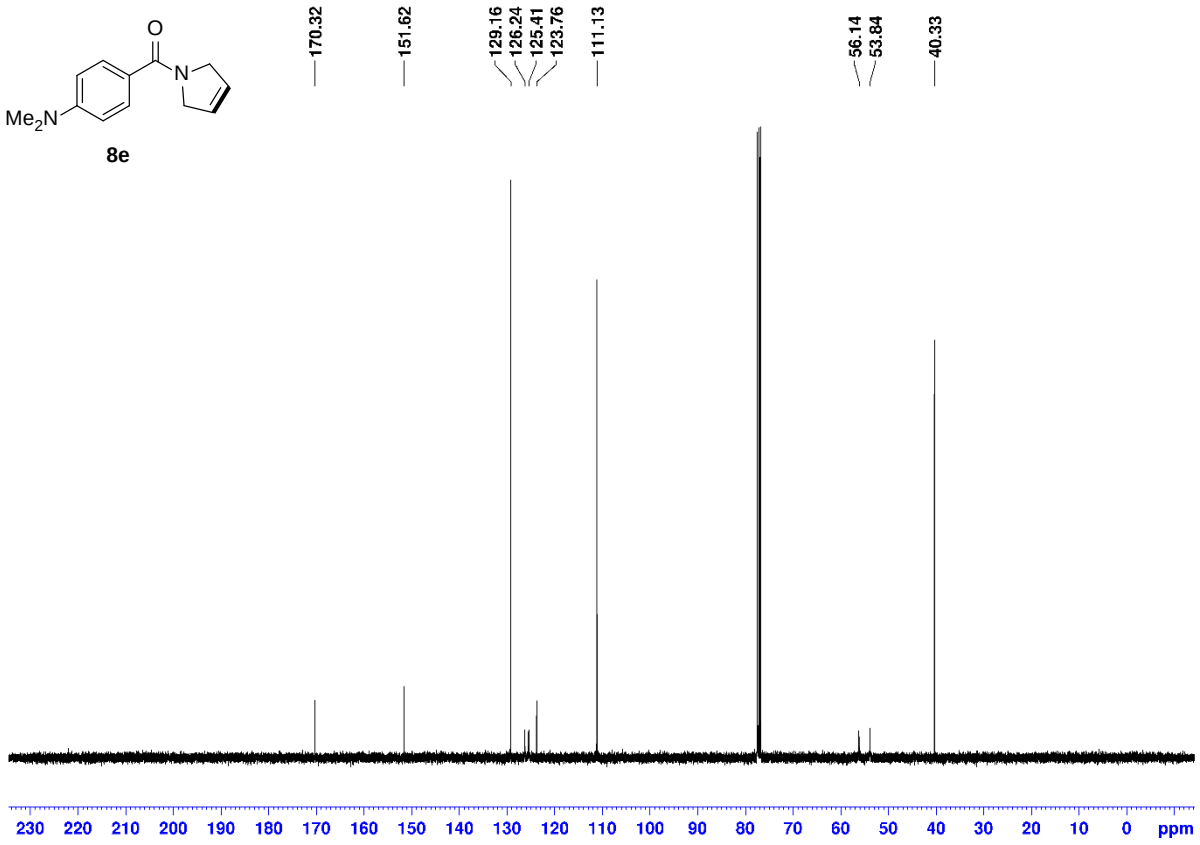
^{13}C NMR (101 MHz), $CDCl_3$



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

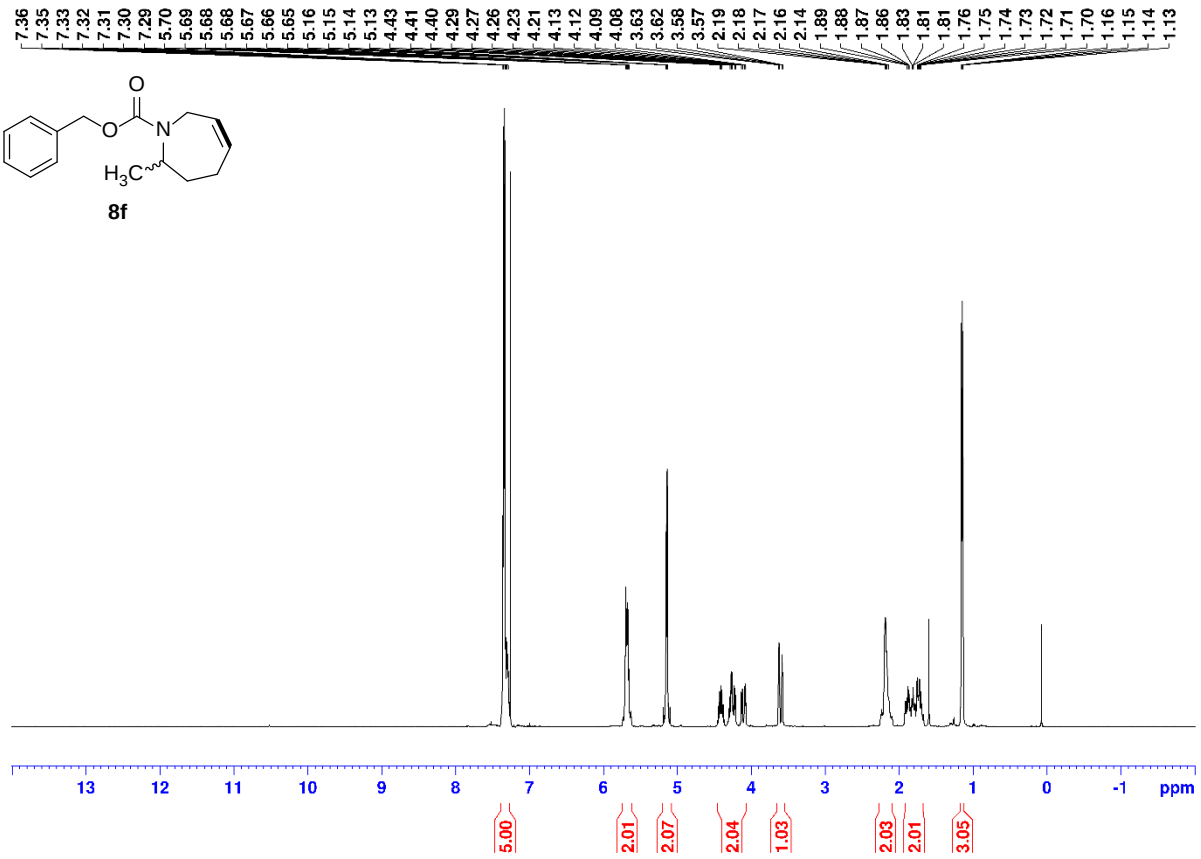


^{13}C NMR (101 MHz), $CDCl_3$



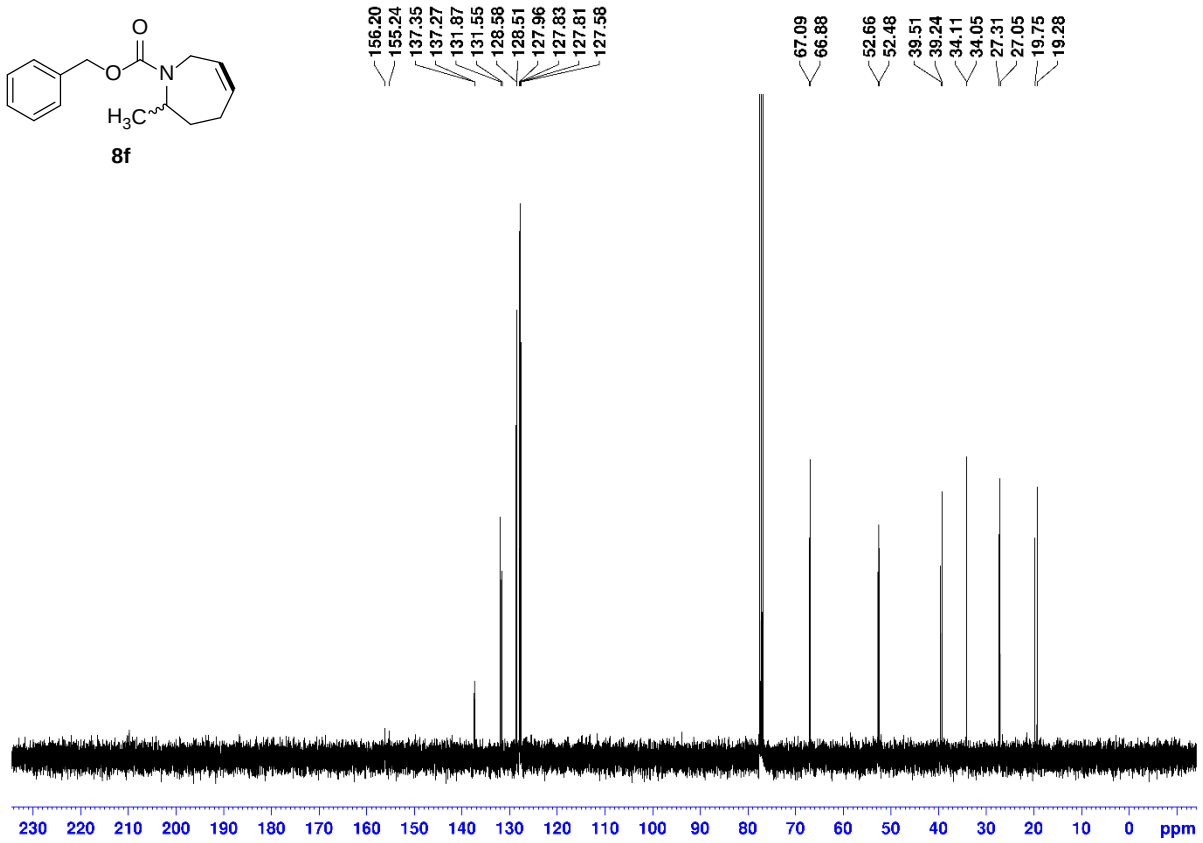
8e

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

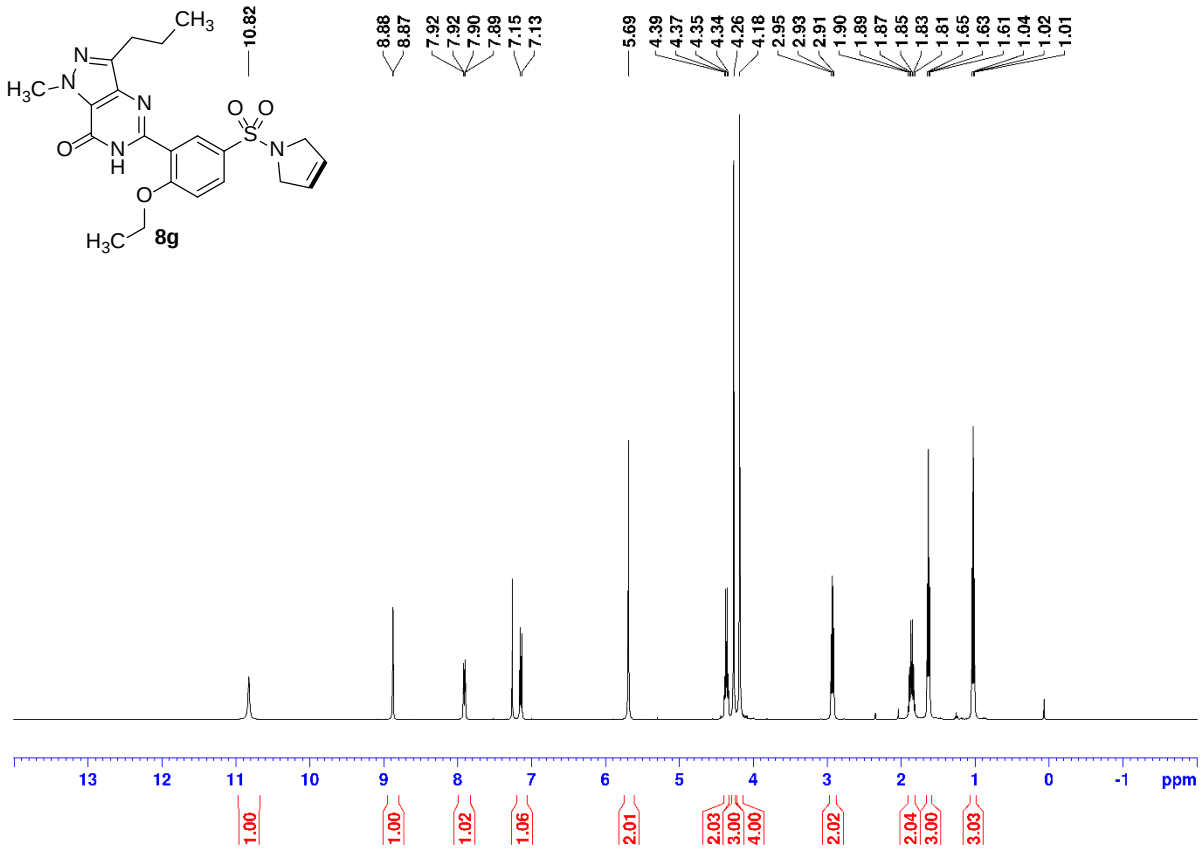


8f

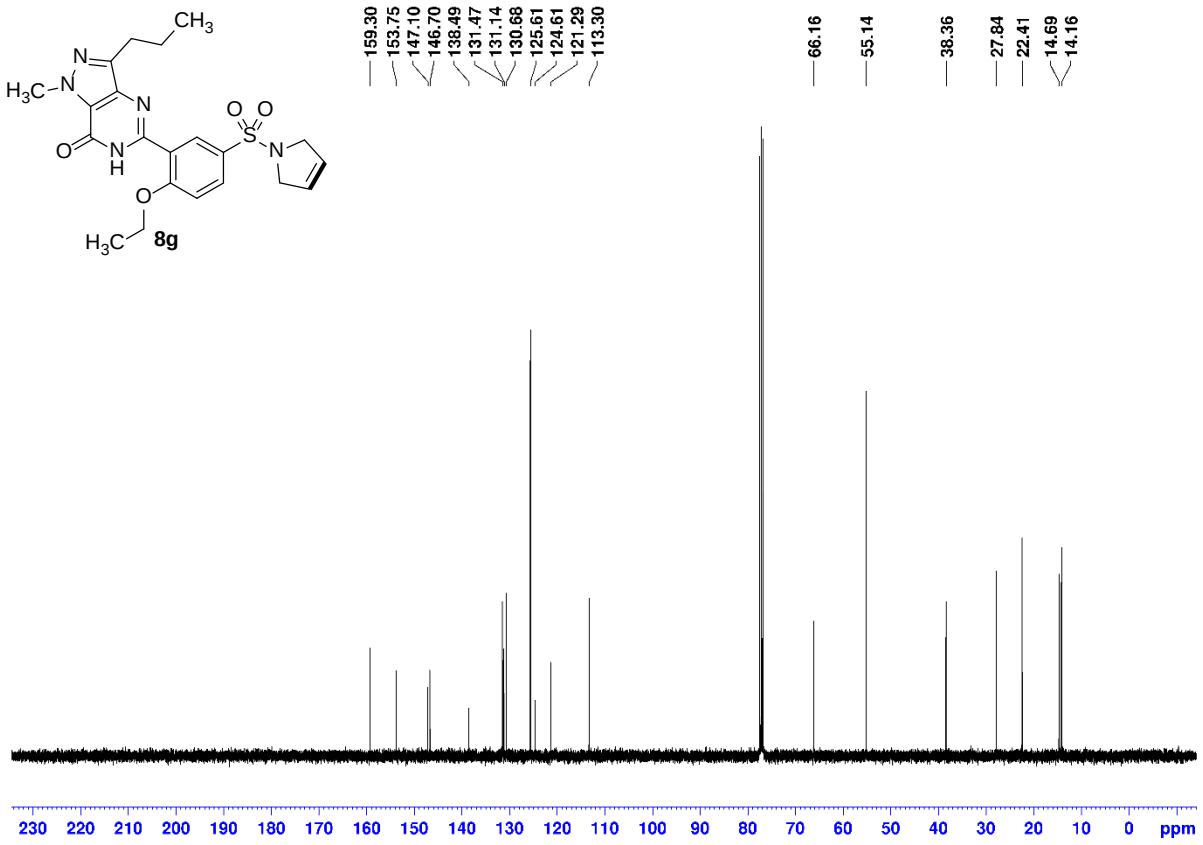
^{13}C NMR (101 MHz), $CDCl_3$



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



^{13}C NMR (101 MHz), $CDCl_3$



8g

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