Supporting Online Material

# Pd-Catalyzed Aryl C–H Imidation with Arene as the Limiting Reagent

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## Materials and Methods

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere, magnetically stirred, and monitored by thin layer chromatography (TLC) using EMD TLC plates pre-coated with 250 μm thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light. Flash chromatography was performed on Dynamic Adsorbents Silica Gel 40–63 μm particle size using a forced flow of eluent at 0.3–0.5 bar pressure.[1] All air- and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under an atmosphere of nitrogen. Acetonitrile and acetonitrile-$d_3$ were dried over $P_2O_5$ and vacuum-distilled. MeOH was degassed at –30 ºC under dynamic vacuum ($10^{-4}$ Torr) for one hour and stored over 3Å sieves. All chemicals were used as received. All deuterated solvents were purchased from Cambridge Isotope Laboratories. NMR spectra were recorded on either a Varian Unity/Inova 600 spectrometer operating at 600 MHz for $^{1}$H acquisitions, a Varian Unity/Inova 500 spectrometer operating at 500 MHz and 125 MHz for $^{1}$H and $^{13}$C acquisitions, respectively, or Varian Mercury 400 spectrometer operating at 375 MHz and 101 MHz for $^{19}$F and $^{13}$C acquisitions, respectively. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($^{1}$H: $CDCl_3$, δ 7.26; $(CD_3)_2SO$, δ 2.50; $(CD_3)_2CO$, δ 2.05; $CD_3CN$, δ 1.94), ($^{13}$C: $CDCl_3$, δ 77.16; $(CD_3)_2SO$, δ 39.52; $(CD_3)_2CO$, δ 29.84; $CD_3CN$, δ 1.32),[2] or added 3-nitrofluorobenzene (–112.0 ppm) for $^{19}$F spectra. Signals are listed in ppm, and multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, quin = quintet, sep = septet, m = multiplet; coupling constants in Hz; integration. High-resolution mass spectra were obtained using an Agilent ESI-TOF (6210) mass spectrometer or a Bruker q-TOF Maxis Impact mass spectrometer. Concentration under reduced pressure was performed by rotary evaporation at 25–30 ºC at appropriate pressure. Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Yields refer to purified and spectroscopically pure compounds.

[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem*. **1978**, *43*, 2925–2927.

[2] Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics*. **2010**, *29*, 2176.

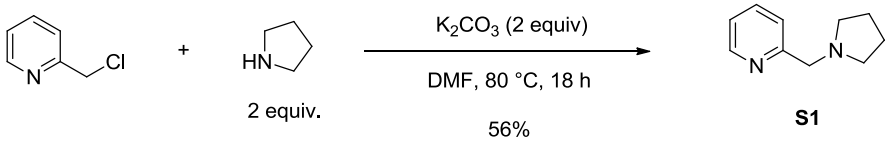
# Experimental Data

## Standard procedure for C–H imidation reactions

Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with (hetero)arene (0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added to react with the remaining NFBS and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel. It was observed that addition of triethylamine to the appropriate solvent system (1% of the final volume) aided the removal of dibenzenesulfonimide, which otherwise co-eluted with the desired product.

## Procedures for preparation of complex 1 and $Ag(bipy)_2ClO_4$

**2-(Pyrrolidin-1-ylmethyl)pyridine (S1)**

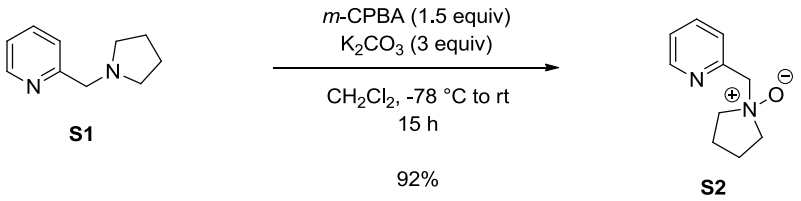



To a solution of 2-(chloromethyl)pyridine (66.2 g, 0.519 mol, 1.00 equiv) in DMF (650 ml, c = 0.800 M) was added potassium carbonate (144 g, 1.04 mol, 2.00 equiv) and the mixture was stirred at 80 °C for 5 min. Pyrrolidine (73.8 g, 1.04 mol, 2.00 equiv) was then added, and the reaction mixture was stirred at 80 °C for 18 h. $H_2O$ (3.50 L) was added and the mixture was extracted with $Et_2O$ (4 × 250 ml). The combined organic layers were washed with $H_2O$ (2 × 200 mL), brine (200 mL), dried ($MgSO_4$), and concentrated *in vacuo* to afford 47.3 g of the title compound as a brown oil (56% yield), which was analytically pure and was used in the next step without further purification.

NMR Spectroscopy: $^1$H NMR (600 MHz, $CD_3CN$, 23 °C, δ): 8.51–8.56 (m, 1H), 7.63 (td, *J* = 7.7, 1.8 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.14 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 3.76 (s, 2H), 2.53–2.60 (m, 4H), 1.76–1.82 (m, 4H). These spectroscopic data correspond to previously reported data.[3]

[3] Sanders, E. B.; Secor, H. V.; Seeman, J. I. *J. Org. Chem.* **1978**, *43*, 324.

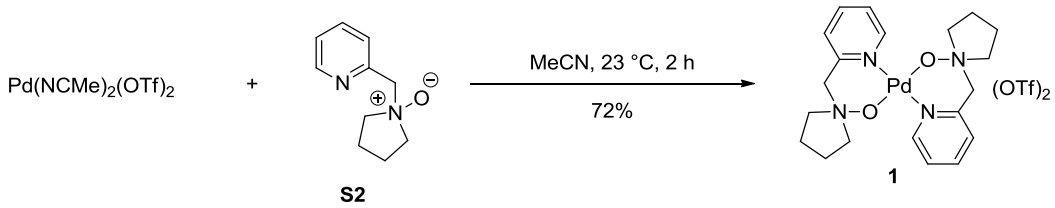
**1-(Pyridin-2-ylmethyl)pyrrolidine 1-oxide (S2)**




To a suspension of $K_2CO_3$ (91.0 g, 0.656 mol, 3.00 equiv) and 2-(pyrrolidin-1-ylmethyl)pyridine (**S1**) (35.5 g, 0.219 mol, 1.00 equiv) in dichloromethane (1.20 L, c = 0.183 M) at –78 °C was added *m*-CPBA (56.6 g, 0.328 mol, 1.50 equiv). The resulting mixture was slowly warmed from –78 °C to 23 °C over 5 h and was stirred at 23 °C for 15 h. The solids were removed by filtration and washed with dichloromethane (3 × 20 mL). The combined filtrates were concentrated *in vacuo* to afford 39.0 g of the title compound (92% yield) as a brown solid, which was used directly for the preparation of **1**. The characterization data was recorded on pure product, which was obtained by triturating the title compound (500 mg) with THF (3 x 2 mL, 15 min each time) at 23 $^{o}$C.

$R_f$ = 0.39 ($CH_2Cl_2$/MeOH 4:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 8.56–8.60 (m, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.77 (td, *J* = 7.6, 1.8 Hz, 1H), 7.31–7.36 (m, 1H), 4.96 (s, 2H), 3.73–3.81 (m, 2H), 3.66–3.73 (m, 2H), 2.29–2.40 (m, 2H), 2.03–2.12 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 150.6, 149.4, 137.2, 128.3, 124.5, 70.8, 67.1, 21.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{10}H_{15}N_2O$ ($[M+ H]^+$), 179.1179, found, 179.1181.

**Palladium complex 1**

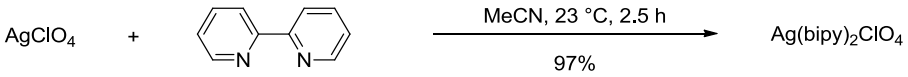



1-(Pyridin-2-ylmethyl)pyrrolidine 1-oxide (**S2**) (3.13 g, 17.6 mmol, 2.00 equiv) and $Pd(MeCN)_4(OTf)_2$ (5.00 g, 8.80 mmol, 1.00 equiv) were dissolved in acetonitrile (70.0 mL, c = 0.125 M). After stirring at 23 °C for 2 h, the reaction mixture was filtered through a pad of celite and the filtrate was concentrated *in vacuo*. The product was triturated with THF (3 x 10 mL, 15 min each time) at 23 $^{o}$C and dried under vacuum for 8 h to afford 4.79 g of the title compound as a light brown solid (72% yield).

Melting point: 188 °C (decomp). NMR Spectroscopy: $^1$H NMR (600 MHz, $CD_3CN$, 23 °C, δ): 8.45 (dd, *J* = 5.9, 1.2 Hz, 2H), 8.20 (td, *J* = 7.6, 1.8 Hz, 2H), 7.71–7.78 (m, 4H), 5.15 (s, 4H), 3.39–3.50 (m, 8H), 2.23–2.32 (m, 4H), 2.05–2.14 (m, 4H). $^{13}$C NMR (125 MHz, $CD_3CN$, 23 °C, δ): 150.5, 149.0, 143.0, 129.3, 127.5, 71.7, 68.9, 22.5. Anal: calcd for $C_{22}H_{28}F_6N_4O_8S_2Pd$: C,

34.72; H, 3.71; N, 7.36; found: C, 34.66; H, 3.42; N, 7.24. UV-VIS Spectroscopy (MeCN, 23 ˚C): 265 nm ($\varepsilon = 1.53 \times 10^3$ $M^{-1}$ $cm^{-1}$); 226 nm ($\varepsilon = 4.77 \times 10^3$ $M^{-1}$ $cm^{-1}$). X-ray data included in X-Ray Crystallographic Analysis Section.

**$Ag(bipy)_2ClO_4$**

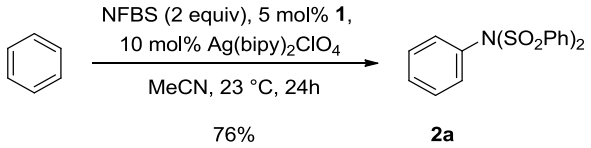



A solution of silver perchlorate (3.27 g, 15.8 mmol, 1.00 equiv) and 2,2'-bipyridine (5.05 g, 32.4 mmol, 2.05 equiv) in acetonitrile (100 mL, c = 0.158 M) was stirred at 23 °C for 2.5 h. The reaction mixture was then concentrated *in vacuo*. The resulting solid was triturated with $Et_2O$ and dried under vacuum to afford 7.93 g of the title compound as a yellow powder (97% yield).

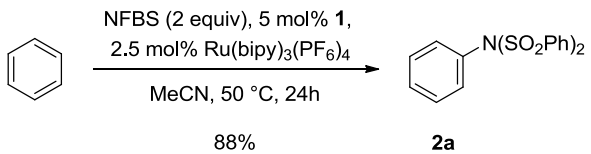
NMR Spectroscopy: $^1$H NMR (600 MHz, $CD_3CN$, 23 °C, δ): 8.66 (dd, *J* = 4.1, 1.8 Hz, 2H), 8.34 (dt, *J* = 8.2, 1.2 Hz, 2H), 8.04 (td, *J* = 7.6, 1.8 Hz, 2H), 7.53–7.56 (m, 2H). $^{13}$C NMR (125 MHz, $CD_3CN$, 23 °C, δ): 153.5, 151.7, 139.9, 126.4, 123.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{20}H_{16}AgN_4^+$ ($Ag(bipy)_2^+$), 419.0420, found, 419.0427.

## Procedures for C–H imidation reactions

**_N_-Phenyl-_N_-(phenylsulfonyl)benzenesulfonamide (2a)**

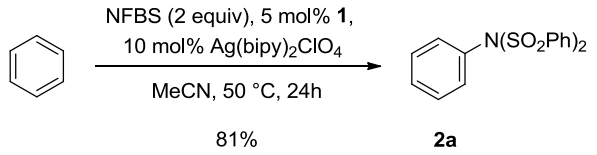



*$Ag(bipy)_2ClO_4$-catalyzed synthesis of **2a**, 23 °C:* Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with benzene (23.4 mg, 26.8 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 (v/v) with 1% triethylamine), to afford 84.7 mg of the title compound as a colorless solid (76% yield).




*$Ru(bipy)_3(PF_6)_2$-catalyzed synthesis of **2a**, 50 °C:* Under $N_2$ atmosphere, an oven-dried 4 mL vial

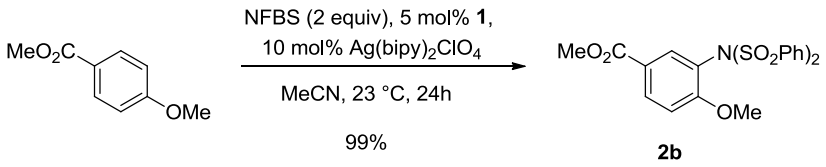
was charged with benzene (39.1 mg, 44.7 µL, 0.500 mmol, 1.00 equiv), palladium complex **1** (19.0 mg, 25.0 µmol, 5.00 mol%), $Ru(bipy)_3(PF_6)_2$ (10.7 mg, 13.0 µmol, 2.5 mol%), and NFBS (0.315 g, 1.00 mmol, 2.00 equiv). Acetonitrile (2.5 mL, c = 0.20 M) was added and the reaction mixture was stirred in a sealed vial at 50 °C for 24 h. Subsequently, triethylamine (50.8 mg, 70.0 µL, 0.500 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 (v/v) with 1% triethylamine), to afford 165 mg of the title compound as a colorless solid (88% yield).




*$Ag(bipy)_2ClO_4$-catalyzed synthesis of **2a**, 50 °C:* Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with benzene (23.4 mg, 26.8 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 50 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 (v/v) with 1% triethylamine), to afford 90.7 mg of the title compound as a colorless solid (81% yield).

$R_f$ = 0.51 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.95 (dd, *J* = 8.8, 1.2 Hz, 4H), 7.66–7.69 (m, 2H), 7.53–7.57 (m, 4H), 7.44–7.47 (m, 1H), 7.34–7.38 (m, 2H), 7.02–7.05 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 139.6, 134.3, 134.1, 131.7, 130.4, 129.4, 129.1, 128.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{18}H_{16}NO_4S_2$ ($[M + H]^+$), 374.0515, found, 374.0524.

**Methyl 4-methoxy-3-(*N*-(phenylsulfonyl)phenylsulfonamido)benzoate (2b)**




Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with methyl 4-methoxybenzoate (49.9 mg, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was

added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 7:3 (v/v) with 1% triethylamine), to afford 137 mg of the title compound as a colorless solid (99% yield).

*Alternative procedure for the preparation of **2b**:* Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with 4-methoxybenzoate (49.9 mg, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (1.5 mL, c = 0.20 M) was added and the reaction mixture was stirred in a sealed vial at 50 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 (v/v) with 1% triethylamine), to afford 97 mg of the title compound as a colorless solid (70% yield).

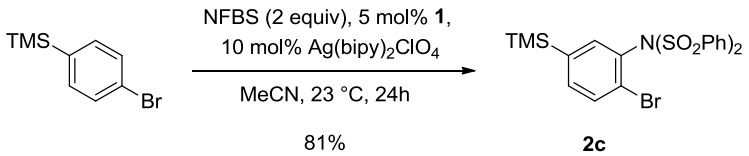
**Preparation of 2b under ambient atmosphere:**

A 4 mL vial was charged with 4-methoxybenzoate (166.2 mg, 1.000 mmol, 1.00 equiv), palladium complex **1** (38.1 mg, 50.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (51.7 mg, 10.0 µmol, 10.0 mol%), and NFBS (636.0 mg, 2.017 mmol, 2.02 equiv). Acetonitrile (2.5 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 (v/v) with 1% triethylamine), to afford 333.7 mg of the title compound as a colorless solid (72% yield).

**Preparation of 2b under nitrogen, with components weighed out under air:**

$R_f$ = 0.56 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 °C, δ): 8.11 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 4H), 7.81 (d, *J* = 2.3 Hz, 1H), 7.62–7.71 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 4H), 6.87 (d, *J* = 8.8 Hz, 1H), 3.88 (s, 3H), 3.44 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 °C, δ): 165.8, 161.3, 140.0, 134.8, 134.0, 133.9, 129.0, 128.9, 123.2, 123.0, 111.7, 55.7, 52.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{21}H_{20}NO_7S_2$ ([M+H]$^+$), 462.0676, found, 462.0690.

***N*-(2-Bromo-5-(trimethylsilyl)phenyl)-*N*-(phenylsulfonyl)benzenesulfonamide (2c)**

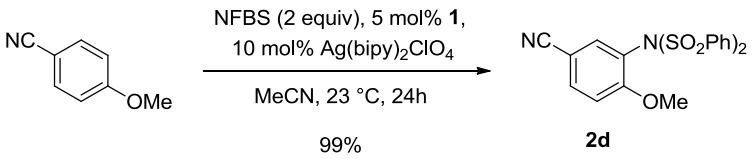



Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with (4-bromophenyl)trimethylsilane (68.8 mg, 58.6 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol,

5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 (v/v) with 1% triethylamine), to afford 128 mg of the title compound as a colorless solid (81% yield).

$R_f$ = 0.57 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 8.00–8.04 (m, 4H), 7.67–7.71 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.53–7.58 (m, 4H), 7.39 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.02 (d, *J* = 1.8 Hz, 1H), 0.18 (s, 9 H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 141.3, 139.5, 138.6, 136.4, 134.3, 134.0, 133.5, 129.5, 129.0, 127.7, –1.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{21}H_{22}BrNNaO_4S_2Si$ $[M + Na]^+$, 547.9815, found, 547.9821.

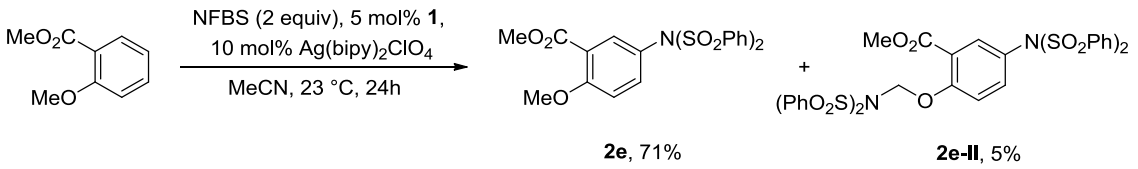
**_N_-(5-Cyano-2-methoxyphenyl)-_N_-(phenylsulfonyl)benzenesulfonamidebenzenesulfonamide (2d)**




Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with 4-methoxybenzonitrile (39.9 mg, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 3:2 (v/v) with 1% triethylamine), to afford 128 mg of the title compound as an off-white solid (99% yield).

$R_f$ = 0.42 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.94 (d, *J* = 8.2 Hz, 4H), 7.66–7.72 (m, 3H), 7.56 (t, *J* = 7.6 Hz, 4H), 7.40 (d, *J* = 2.3 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 3.44 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 161.3, 139.7, 137.0, 136.4, 134.2, 129.0, 128.9, 124.1, 117.9, 112.9, 104.7, 55.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{20}H_{17}N_2O_5S_2$ ($[M + H]^+$), 429.0573, found, 429.0566.

**Methyl 2-methoxy-5-(_N_-(phenylsulfonyl)phenylsulfonamido)benzoate (2e)**

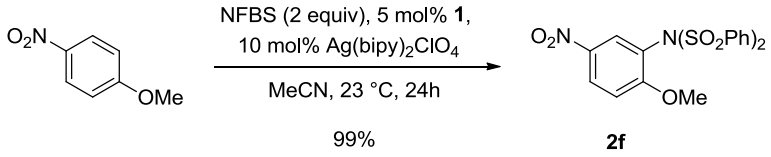


Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with methyl 2-methoxybenzoate (49.9 mg, 43.1 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 7:3 (v/v) with 1% triethylamine), to afford 110 mg of the mixture of the title compound and methyl 5-(*N*-(henylsulfonyl)phenylsulfonamido)-2-((*N*-(phenylsulfonyl)phenylsulfonamido)methoxy)benzoate (**2e-II**) (76% yield). Purification for characterization was accomplished by preparative TLC.

Data for **2e**: colorless solid; $R_f$ = 0.31 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.90–7.94 (m, 4H), 7.66–7.70 (m, 2H), 7.53–7.58 (m, 4H), 7.44 (d, *J* = 2.3 Hz, 1H), 7.11 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 1H), 3.92 (s, 3H), 3.82 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 165.1, 160.5, 139.3, 136.5, 135.0, 134.2, 129.2, 128.6, 126.1, 120.7, 112.6, 56.4, 52.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{21}H_{20}NO_7S_2$ $[M + H]^+$, 462.0676, found, 462.0686.

Data for **2e-II**: colorless solid; NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 8.04–8.07 (m, 4H), 7.91–7.93 (m, 4H), 7.64–7.73 (m, 4H), 7.51– 7.59 (m, 9H), 7.01–7.06 (m, 1H), 6.79–6.83 (m, 1H), 5.83 (s, 2H), 3.72 (s, 3H).

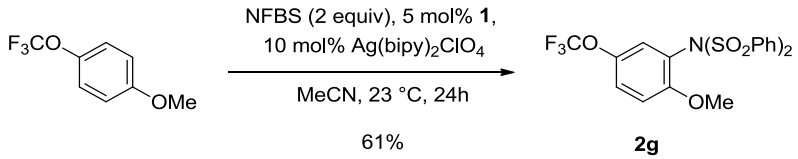
**_N_-(2-Methoxy-5-nitrophenyl)-_N_-(phenylsulfonyl)benzenesulfonamide (2f)**




Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with 1-methoxy-4-nitrobenzene (45.9 mg, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 1:1 (v/v) with 1% triethylamine), to afford 134 mg of the title compound as an off-white solid (99% yield).

$R_f$ = 0.27 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 8.34 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.99 (d, *J* = 2.9 Hz, 1H), 7.96 (dt, *J* = 7.0, 1.8 Hz, 3H), 7.70 (tt, *J* = 7.6, 1.2 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 4H), 6.94 (d, *J* = 9.4 Hz, 1H), 3.52 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 162.9, 141.2, 139.7, 134.3, 129.3, 129.1, 128.9, 128.0, 123.6, 111.7, 56.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{19}H_{17}N_2O_7S_2$ ($[M+ H]^+$), 449.0472, found, 449.0484.

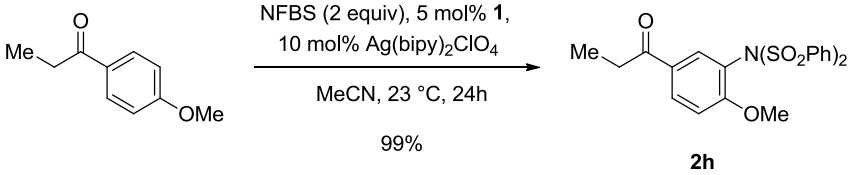
***N*-(2-Methoxy-5-(trifluoromethoxy)phenyl)-*N*-(phenylsulfonyl)benzenesulfonamide (2g)**




Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with 1-methoxy-4-(trifluoromethoxy)benzene (57.6 mg, 45.5 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 (v/v) with 1% triethylamine), to afford 89.2 mg of the title compound as a colorless solid (61% yield).

$R_f$ = 0.30 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.97 (d, *J* = 7.6 Hz, 4H), 7.65–7.69 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 4H), 7.29 (dd, *J* = 9.5, 2.9 Hz, 1H), 6.95 (d, *J* = 2.9 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 3.43 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 156.8, 141.8, 139.8, 134.0, 128.9, 128.9, 126.5, 125.1, 123.4, 120.6 (q, *J* = 255 Hz), 112.4, 55.8. $^{19}$F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –59.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{20}H_{20}F_3N_2O_6S_2$ $[M + NH_4]^+$, 505.0709, found, 505.0721.

***N*-(2-Methoxy-5-propionylphenyl)-*N*-(phenylsulfonyl)benzenesulfonamide (2h)**

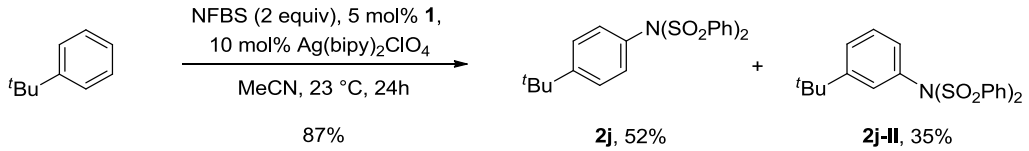



Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with 1-(4-methoxyphenyl)propan-1-one (49.2 mg, 45.7 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 7:3 (v/v) with 1% triethylamine), to afford 136 mg of the title compound as a colorless solid (99% yield).

$R_f$ = 0.33 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 8.05 (dd, *J* = 6.5, 2.3 Hz, 1H), 7.93–7.97 (m, 4H), 7.64–7.68 (m, 3H), 7.54 (t, *J* = 8.2 Hz, 4H), 6.89 (d, *J* = 8.8 Hz, 1H), 3.45 (s, 3H), 2.84 (q, *J* = 7.0 Hz, 2H), 1.18 (t, *J* = 7.0 Hz, 3H). $^{13}$C

NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 198.2, 161.2, 139.9, 134.0, 133.4, 132.4, 130.2, 128.9, 128.8, 122.9, 111.8, 55.7, 31.6, 8.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{22}H_{21}NNaO_6S_2$ ($[M + Na]^+$), 482.0702, found, 482.0716.

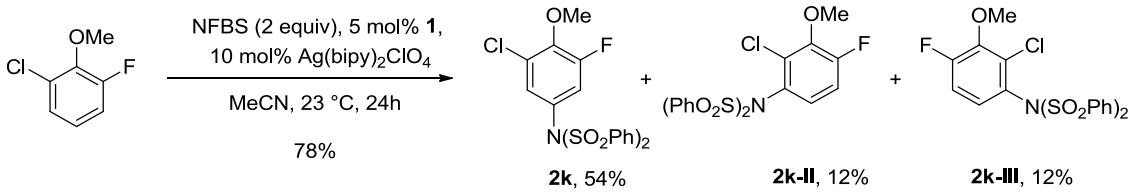
**_N_-(4-(_tert_-Butyl)phenyl)-_N_-(phenylsulfonyl)benzenesulfonamide (2j) and _N_-(3-(_tert_-Butyl)phenyl)-_N_-(phenylsulfonyl)benzenesulfonamide (2j-II)**




Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with *tert*-butylbenzene (40.3 mg, 46.4 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (9:1 (v/v) with 1% triethylamine), to afford 112.0 mg of the mixture of the title compounds as a colorless solid (87% yield).

The products could not readily be separated by silica gel chromatography or preparative TLC, so they were characterized as a mixture. Data for **2j** and **2j-II**: $R_f$ = 0.63 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.94–7.97 (m, 10H), 7.65–7.69 (m, 5H), 7.52–7.58 (m, 10H), 7.44–7.48 (m, 1H), 7.34–7.38 (m, 3H), 7.29–7.33 (m, 1H), 6.92–6.97 (m, 4H), 6.84 (t, *J* = 2.1 Hz, 1H), 1.33 (s, 13.5H), 1.20 (s, 9H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 153.7, 152.5, 139.7, 139.7, 134.1, 134.0, 134.0, 131.5, 131.0, 129.1, 129.0, 128.7, 128.7, 128.5, 127.3, 126.4, 35.0, 34.7, 31.4, 31.1. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{22}H_{27}N_2O_4S_2$ ($[M + NH_4]^+$), 447.1407, found, 447.1399.

**_N_-(3-Chloro-5-fluoro-4-methoxyphenyl)-_N_-(phenylsulfonyl)benzenesulfonamide (2k)**

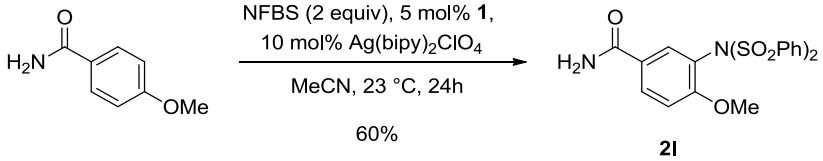



Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with 1-chloro-3-fluoro-2-methoxybenzene (48.2 mg, 38.9 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The

residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 (v/v) with 1% triethylamine), to afford 106.7 mg of a mixture of the title compound and its two constitutional isomers (78% yield). Purification for characterization was accomplished by preparative TLC.

Data for **2k**: colorless solid; $R_f$ = 0.59 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.93–7.97 (m, 4H), 7.70–7.74 (m, 2H), 7.57–7.61 (m, 4H), 6.83 (t, *J* = 2.1 Hz, 1H), 6.72 (dd, *J* = 10.9, 2.6 Hz, 1H), 4.04 (d, *J* = 2.3 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 155.1 (d, *J* = 251.3 Hz), 146.4 (d, *J* = 12.5 Hz), 139.1, 134.5, 129.4, 129.1 (d, *J* = 3.8 Hz), 128.8 (d, *J* = 1.1 Hz), 128.7, 128.4 (d, *J* = 5.5 Hz), 119.4 (d, *J* =20 Hz), 61.7 (d, *J* = 6.3 Hz). $^{19}$F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –129.0 (d, *J* = 9.8 Hz). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{19}H_{19}ClFN_2O_5S_2$ $[M + NH_4]^+$, 473.0402, found, 473.0415.

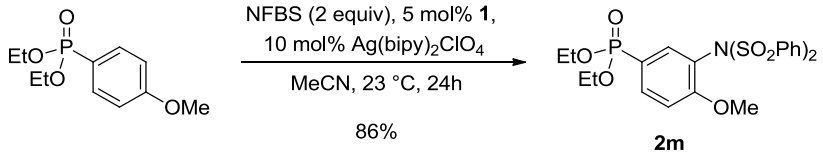
**4-Methoxy-3-(*N*-(phenylsulfonyl)phenylsulfonamido)benzamide (2l)**




Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with 4-methoxybenzamide (45.3 mg, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (1:4 (v/v) with 1% triethylamine), to afford 80.0 mg of the title compound as an off-white solid (60% yield).

$R_f$ = 0.39 (EtOAc). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.94–7.98 (m, 5H), 7.65–7.69 (m, 2H), 7.52–7.56 (m, 4H), 7.50 (d, *J* = 2.3 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 3.45 (s, 3H). $^{13}$C NMR (125 MHz, $(CD_3)_2CO$, 23 ºC, δ): 167.2, 160.9, 140.9, 134.9, 133.7, 132.6, 129.7, 129.6, 127.8, 123.4, 112.6, 55.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{20}H_{19}N_2O_6S_2$ ($[M + H]^+$), 447.0679, found, 447.0684.

**Diethyl (4-methoxy-3-(*N*-(phenylsulfonyl)phenylsulfonamido)phenyl)phosphonate (2m)**

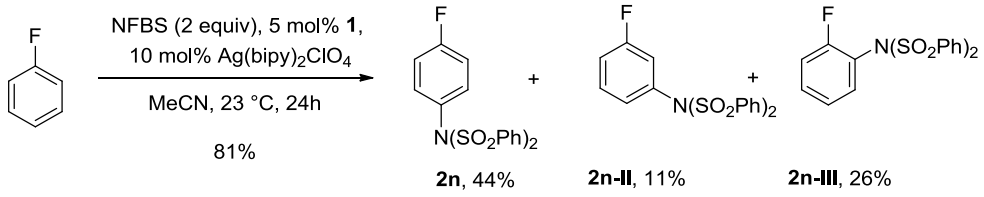



Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with diethyl (4-

methoxyphenyl)phosphonate (73.3 mg, 65.4 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (3:2 to 1:9 (v/v) with 1% triethylamine), to afford 138.4 mg of the title compound as a colorless solid (86% yield).

$R_f$ = 0.52 (EtOAc). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.92–7.94 (m, 4H), 7.88 (ddd, *J* = 12.8, 8.4, 1.8 Hz, 1H), 7.63–7.67 (m, 2H), 7.52 (t, *J* = 7.9 Hz, 4H), 7.46 (dd, *J* = 13.2, 2.1 Hz, 1H), 6.91 (dd, *J* = 8.5, 3.8 Hz, 1H), 4.00–4.14 (m, 4H), 3.44 (s, 3H), 1.30 (t, *J* = 7.3 Hz, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 160.8 (d, *J* = 3.4 Hz), 139.9, 136.8 (d, *J* = 10.0 Hz), 136.3 (d, *J* = 10.0 Hz), 133.9, 128.9, 128.8, 123.2 (d, *J* = 20.0 Hz), 120.6 (d, *J* = 193.4 Hz), 112.1 (d, *J* = 17.5 Hz), 62.3 (d, *J* = 5.0 Hz), 55.6, 16.4 (d, *J* = 6.3 Hz). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{23}H_{27}NO_8PS_2$ $[M + H]^+$, 540.0910, found, 540.0922.

***N*-(4-Fluorophenyl)-*N*-(phenylsulfonyl)benzenesulfonamide (2n)**



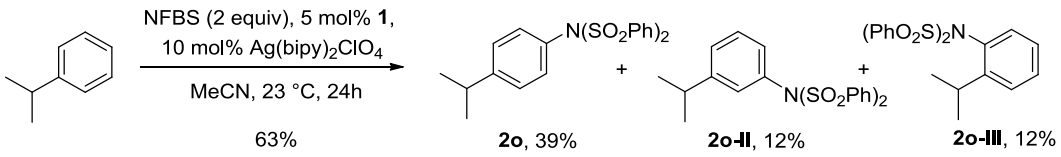

Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with fluorobenzene (28.8 mg, 28.2 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 (v/v) with 1% triethylamine), to afford two fractions: fraction A (36.9 mg) contained a 7.1:1 ratio of **2n**:**2n-II**, and fraction B (58.6 mg) contained a 1.35:1:2.35 ratio of **2n**:**2n-II**:**2n-III**. The total yield is therefore 95.5 mg (81% yield) with a product ratio of **2n**:**2n-II**:**2n-III** = 4:1:2.3.

The major component (**2n**) was further separated for characterization from fraction A by column chromatography eluting with hexanes/EtOAc (19:1 to 4:1 (v/v). Compound **2n-II** was assigned by COSY of the mixture in fraction A (see S87 for details). Compound **2n-III** was assigned by process of elimination. Data for **2n**:

$R_f$ = 0.47 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.95–7.92 (m, 4H), 7.71–7.67 (m, 2H), 7.58–7.54 (m, 4H), 7.07–7.02 (m, 2H), 7.02–6.98 (m, 2H),. $^{13}$C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 166.1 (d, *J* = 252.6 Hz), 139.2 (s), 134.3 (s), 134.1

(s), 133.5 (d, $J$ = 9.3 Hz), 130.1 (s), 128.8 (d, $J$ = 54.4 Hz), 116.4 (d, J = 23.2). $^{19}$F NMR (125 MHz, $CDCl_3$, 23 ºC, δ): -108.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{18}H_{15}FNO_4S_2$ ($[M + H]^+$), 392.0421, found, 392.0416.

***N*-(4-*iso*Propylphenyl)-*N*-(phenylsulfonyl)benzenesulfonamide (2o)**

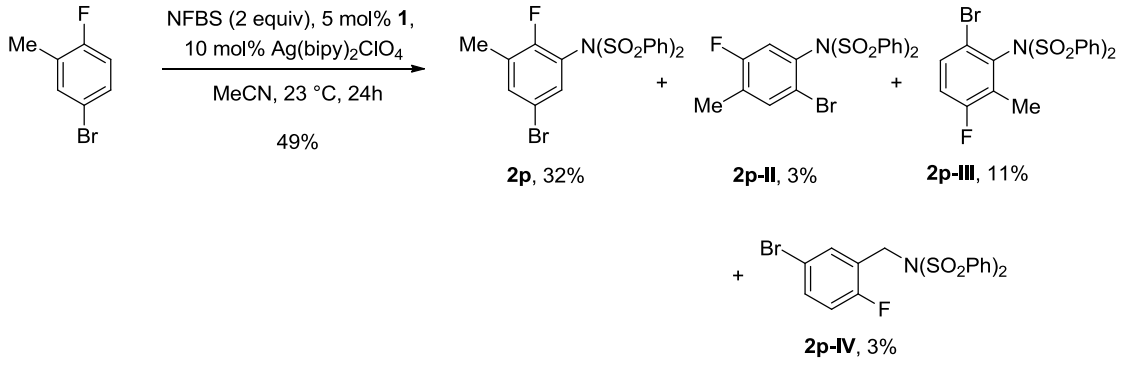



Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with cumene (36.1 mg, 40.3 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 with 1% triethylamine), to afford 78.4 mg of the mixture of the title compounds as a yellow solid (63% yield).

The products could not readily be separated by silica gel chromatography or preparative TLC, so they were characterized as a mixture. Data for **2o** and **2o-II** and **2o-III**:

$R_f$ = 0.54 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.00–7.90 (m, 6.7H), 7.71–7.64 (m, 3.5H), 7.59–7.50 (m, 6.8H), 7.44–7.36 (m, 0.9H), 7.32–7.28 (m, 0.6H), 7.24–7.17 (m, 2H), 7.12–7.16 (m, 0.4H), 6.97–6.88 (m, 2.3H), 6.81–6.72 (m, 0.6H), 3.02 (sept, 0.3H), 2.94 (sept, 1H), 2.83 (sept, 0.3H), 1.26 (d, 6H), 1.14 (d, 1.9H), 1.04 (d, 1.9H). $^{13}$C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 151.3, 151.2, 150.0, 139.6, 139.5, 139.2, 134.1, 134.0, 133.8, 131.6, 131.4, 131.2, 130.7, 129.6, 129.0, 128.9, 128.8, 128.6, 128.5, 127.7, 127.3, 125.9, 33.8, 33.6, 28.4, 24.0, 23.7, 23.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{21}H_{21}NO_4S_2$ ($[M + H]^+$), 416.0985, found, 416.0986.

***N*-(4-*iso*Propylphenyl)-*N*-(phenylsulfonyl)benzenesulfonamide (2p)**



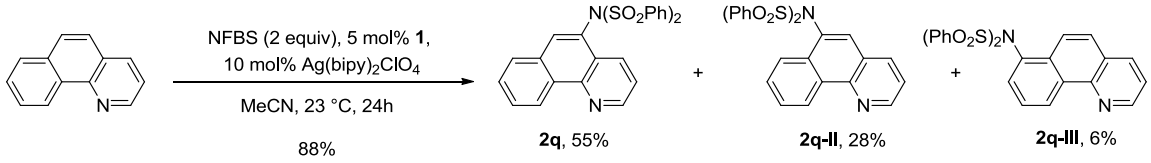

Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with 2-fluoro-5-bromotoluene (56.7

mg, 38.3 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 with 1% triethylamine), to afford 71.0 mg of the mixture of the title compounds as a yellow solid (63% yield).

The products could not readily be separated by silica gel chromatography or preparative TLC, so they were characterized as a mixture. Compounds **2p–2p-IV** were assigned through a combination of 1-D TOCSY and NOESY experiments (see page S92–S93). Data for **2p** and **2p-II** and **2p-III**:

$R_f$ = 0.57 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 8.07 (d, *J* = 8.2 Hz, 1.3H), 8.00 (d, *J* = 8.2 Hz, 4H), 7.96 (d, *J* = 8.2 Hz, 0.4H), 7.91 (d, *J* = 8.2 Hz, 0.6H), 7.72–7.68 (m, 2.9H), 7.66–7.62 (m, 0.3H), 7.59–7.54 (m, 5.7H), 7.53–7.49 (m, 0.7H), 7.46–7.42 (m, 1.5H), 7.31–7.27 (m, 0.2H), 7.25–7.22 (m, 0.2H), 7.01 (dd, *J* = 8.7, 8.7 Hz, 0.45H), 6.87 (dd, *J* = 9.6, 9.6 Hz, 0.2H), 6.81 (d, *J* = 9.6 Hz, 1H), 5.01 (s, 0.3H), 2.30 (s, 3H), 2.21 (s, 0.2H), 1.84 (s, 1.0H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): Peaks are not listed because the mixture of four compounds, as well as splitting of aryl carbons by $^{19}$F, precluded assignment. See S91 for spectrum. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{19}H_{15}BrNNaO_4S_2$ ($[M + Na]^+$), 505.9504, found, 505.9502.

**N-(Benzo[h]quinolin-5-yl)-N-(phenylsulfonyl)benzenesulfonamide (2q)**

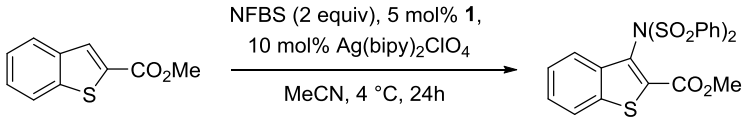



Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with benzo[*h*]quinoline (56.7 mg, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 (v/v) with 1% triethylamine), to afford 27.5 mg of the title compound as a colorless solid, along with 97.6 mg of a 6.7:4.3:1 mixture of **2q**, **2q-II**, and **2q-III** (88% yield overall). Compounds **2q-II** and **2q-III** were separated from **2q** by preparative thin layer chromatography (eluting twice with 1:4 EtOAc:hexanes), and were assigned as a mixture through a combination of one-dimensional TOCSY and NOESY NMR experiments (see page S97). Data for **2q**:

$R_f$ = 0.47 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ):

9.32 (d, J = 8.7 Hz, 1H), 8.96 (dd, *J* = 4.3 Hz, 1.7 Hz, 1H), 7.96 (dd, J = 7.96, 1.0 Hz, 4H), 7.88 (dd, J = 8.5, 1.8 Hz, 1H), 7.83 (ddd, J = 8.1, 6.7, 1.4 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.72 (m, 3H), 7.54 (m, 4 H), 7.46 (s, 1H), 7.31 (dd, *J* = 8.1, 4.4 Hz. 1H); $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 149.3, 147.0, 138.8, 134.3, 132.8, 132.6, 132.3, 131.9, 129.1, 129.0, 128.8, 128.6, 128.5, 125.8, 124.7, 121.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{25}H_{18}N_2NaO_4S_2$ ($[M + Na]^+$), 497.0600, found, 497.0595.

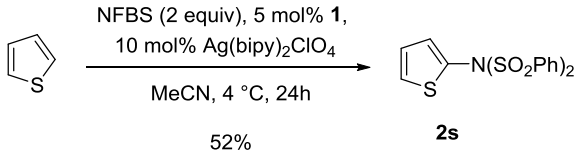
**Methyl 3-(*N*-(phenylsulfonyl)phenylsulfonamido)benzo[*b*]thiophene-2-carboxylate (2r)**




Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with methyl benzo[*b*]thiophene-2-carboxylate (27.7 mg, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 4 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 (v/v) with 1% triethylamine), to afford 115 mg of the title compound as a colorlesssolid (79% yield).

$R_f$ = 0.38 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.98–8.00 (m, 4H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.66–7.70 (m, 2H), 7.53 (t, *J* = 7.9 Hz, 4H), 7.46 (td, *J* = 7.6, 1.2 Hz, 1H), 7.30–7.33 (m, 1H), 7.25–7.28 (m, 1H), 3.39 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 160.9, 139.8, 138.2, 137.4, 134.6, 134.2, 129.4, 128.9, 128.8, 127.8, 125.4, 124.8, 122.8, 52.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{22}H_{21}N_2O_6S_3$ [M + $NH_4]^+$, 505.0556, found, 505.0569.

***N*-(Phenylsulfonyl)-*N*-(thiophen-2-yl)benzenesulfonamide (2s)**

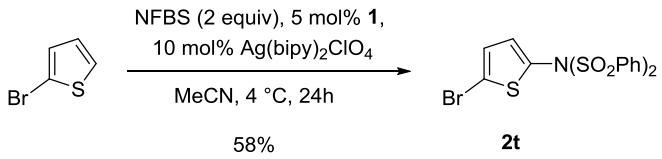



Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with thiophene (25.2 mg, 24.4 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 4 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on

silica gel, eluting with hexanes/EtOAc (99:1 to 5.6:1 (v/v) with 1% triethylamine), to afford 59.7 mg of the title compound as a colorless solid (52% yield).

$R_f$ = 0.53 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.99 (dd, *J* = 8.3, 1.1 Hz, 4H), 7.68–7.71 (m, 2H), 7.55–7.59 (m, 4H), 7.38 (dd, *J* = 5.5, 1.7 Hz, 1H), 6.94 (dd, *J* = 5.5, 3.9 Hz, 1H), 6.74 (dd, *J* = 3.9, 1.1 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 138.8, 134.4, 134.0, 131.4, 129.2, 128.9, 128.8, 125.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{16}H_{13}NNaO_4S_3$ ($[M + Na]^+$), 401.9899, found, 401.9913.

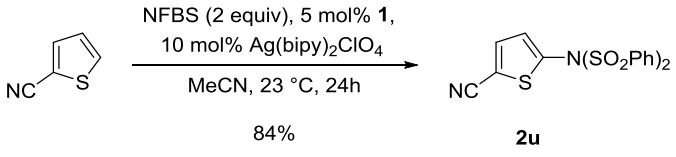
***N*-(5-Bromothiophen-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (2t)**




Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with 2-bromothiophene (48.9 mg, 29.0 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 4 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 (v/v) with 1% triethylamine), to afford 80.3 mg of the title compound as a colorless solid (58% yield).

$R_f$ = 0.52 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.97–8.02 (m, 4H), 7.71 (t, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.9 Hz, 4H), 6.94 (d, *J* = 4.1 Hz, 1H), 6.50 (d, *J* = 4.1 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 138.6, 134.6, 134.3, 132.3, 129.3, 128.9, 128.8, 115.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{16}H_{12}BrNNaO_4S_3$ $[M + Na]^+$, 481.8983, found, 481.8987.

***N*-(5-Cyanothiophen-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (2u)**

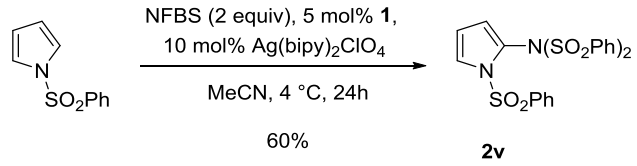



Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with thiophene-2-carbonitrile (27.9 µL, 32.7 mg, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol,

1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 (v/v) with 1% triethylamine), to afford 102 mg of the title compound as a colorlesssolid (84% yield).

$R_f$ = 0.41 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.97 (d, *J* = 7.6 Hz, 4H), 7.74 (t, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.9 Hz, 4H), 7.46 (d, *J* = 4.1 Hz, 1H), 6.77 (d, *J* = 4.1 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 140.3, 138.1, 135.8, 135.0, 131.6, 129.5, 128.9, 113.2, 112.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{17}H_{12}N_2NaO_4S_3$ ([M + Na]$^+$), 426.9851, found, 426.9861.

**_N_-(Phenylsulfonyl)-_N_-(1-(phenylsulfonyl)-1H-pyrrol-2-yl)benzenesulfonamide (2v)**

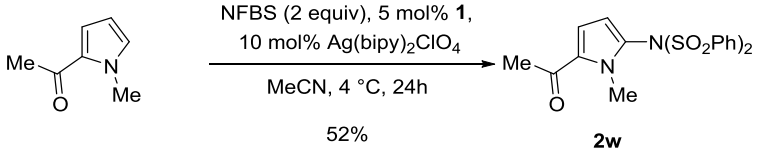



**2v**

Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with methyl 1-(phenylsulfonyl)-1H-pyrrole (62.2 mg, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 4 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 4:1 (v/v) with 1% triethylamine), to afford 90.5 mg of the title compound as a colorless solid (60% yield).

$R_f$ = 0.46 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.95–7.99 (m, 6H), 7.67–7.70 (m, 2H), 7.58–7.61 (m, 1H), 7.52–7.56 (m, 4H), 7.47–7.51 (m, 2H), 7.22 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.26 (t, *J* = 3.5 Hz, 1H), 6.04 (dd, *J* = 3.5, 1.8 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 139.0, 138.4, 134.4, 134.3, 129.8, 129.1, 128.9, 128.5, 124.8, 122.6, 117.7, 111.0. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{22}H_{19}N_2O_6S_3$ ([M + H]$^+$), 503.0400, found, 503.0397.

**_N_-(5-Acetyl-1-methyl-1*H*-pyrrol-2-yl)-_N_-(phenylsulfonyl)benzenesulfonamide (2w)**



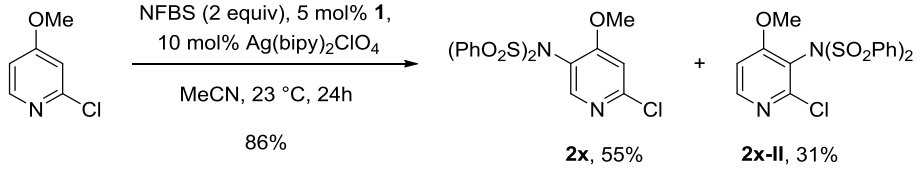

**2w**

Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with 1-(1-methyl-1H-pyrrol-2-yl)ethanone (36.9 mg, 35.5 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600

mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 4 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 3:1 (v/v) with 1% triethylamine), to afford 65.8 mg of the title compound as a colorless solid (52% yield).

$R_f$ = 0.46 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.90–7.94 (m, 4H), 7.68–7.72 (m, 2H), 7.56 (t, *J* = 8.2 Hz, 4H), 6.89 (d, *J* = 4.7 Hz, 1H), 5.92 (d, *J* = 4.1 Hz, 1H), 3.42 (s, 3H), 2.44 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 189.1, 138.7, 134.7, 131.4, 129.3, 128.9, 127.5, 117.5, 111.4, 33.1, 27.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{19}H_{19}N_2O_5S_2$ ($[M + H]^+$), 419.0730, found, 419.0734.

**_N_-(6-Chloro-4-methoxypyridin-3-yl)-_N_-(phenylsulfonyl)benzenesulfonamide (2x) and _N_-(2-Chloro-4-methoxypyridin-3-yl)-_N_-(phenylsulfonyl)benzenesulfonamide (2x-II)**



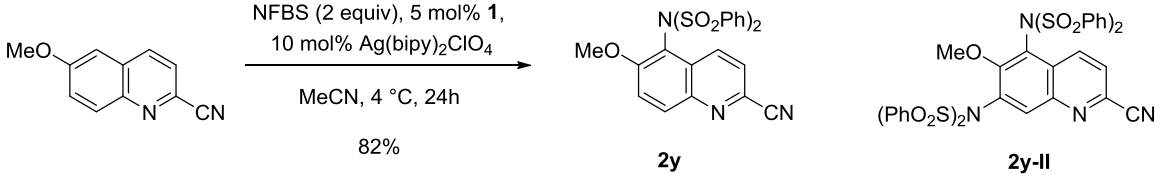

Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged 2-chloro-4-methoxypyridine (43.1 mg, 34.2 µL, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (7:3 to 2:3 (v/v) with 1% triethylamine), to afford 72.4 mg (55% yield) of **2x** and 40.2 mg (31% yield) of **2x-II**.

Data for **2x**: yellow solid; $R_f$ = 0.61 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.94–7.98 (m, 4H), 7.91 (s, 1H), 7.66–7.71 (m, 2H), 7.54–7.58 (m, 4H), 6.82 (s, 1H), 3.50 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 164.8, 154.7, 152.3, 139.6, 134.3, 129.1, 128.9, 120.6, 108.2, 56.1. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{18}H_{16}ClN_2O_5S_2$ ($[M + H]^+$), 439.0184, found, 439.0200.

Data for **2x-II**: yellow oil; $R_f$ = 0.22 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 8.29 (d, *J* = 5.9 Hz, 1H), 8.03 – 8.06 (m, 4H), 7.65–7.69 (m, 2H), 7.55 (t, *J* = 7.9 Hz, 4H), 6.77 (d, *J* = 5.9 Hz, 1H), 3.46 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 165.9, 155.0, 151.5, 139.9, 134.2, 129.5, 128.8, 119.1, 107.2, 56.2. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{18}H_{16}ClN_2O_5S_2$ ($[M + H]^+$), 439.0184, found, 439.0184.

**_N_-(6-Methoxy-2-methylquinolin-7-yl)-_N_-(phenylsulfonyl)benzenesulfonamide (2y) and**

**_N_,_N_'-(6-Methoxy-2-methylquinoline-5,7-diyl)bis(_N_-(phenylsulfonyl)benzenesulfonamide) (2y-II)**

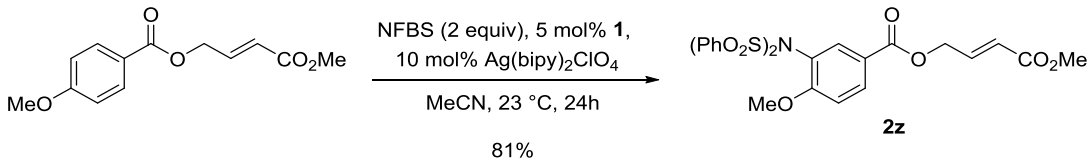



Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with 6-methoxyquinoline-2-carbonitrile (55.3 mg, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 4 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 1:1 (v/v) with 1% triethylamine), to afford 115 mg of the title compound (82% yield). When the reaction was performed at 23 °C, a 6:5 mixture of **2y** and **2y-II** was formed in 77% yield.

Data for **2y**: colorless solid; $R_f$ = 0.33 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 8.28 (d, *J* = 9.4 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.91 (dd, *J* = 8.8, 1.2 Hz, 4H), 7.68–7.72 (m, 2H), 7.52–7.56 (m, 5H), 7.51 (d, *J* = 2.9 Hz, 1H), 3.49 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 158.4, 143.9, 139.6, 134.9, 134.3, 133.4, 131.9, 130.5, 129.3, 128.9, 124.4, 117.8, 117.5, 115.8, 56.1. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{23}H_{18}N_3O_5S_2$ ($[M + H]^+$), 480.0682, found, 480.0695.

Data for **2y-II**: colorless solid; $R_f$ = 0.40 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 8.03 (d, *J* = 8.2 Hz, 1H), 7.88 (dd, *J* = 8.8, 1.2 Hz, 4H), 7.85 (dd, *J* = 8.8, 1.2 Hz, 4H), 7.70–7.74 (m, 2H), 7.64–7.68 (m, 2H), 7.53–7.57 (m, 5H), 7.48–7.52 (m, 4H), 7.40 (d, *J* = 8.8 Hz, 1H), 3.42 (s, 3 H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 157.8, 141.2, 139.2, 138.3, 135.6, 134.5, 134.0, 131.7, 130.8, 129.5, 129.3, 129.0, 128.9, 124.7, 123.6, 118.1, 116.5, 56.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{35}H_{27}N_4O_9S_4$ ($[M + H]^+$), 775.0655, found, 775.0668.

**(*E*)-4-methoxy-4-oxobut-2-en-1-yl-4-methoxy-3-(*N*-(phenylsulfonyl)phenylsulfonamido) benzoate (2z)**

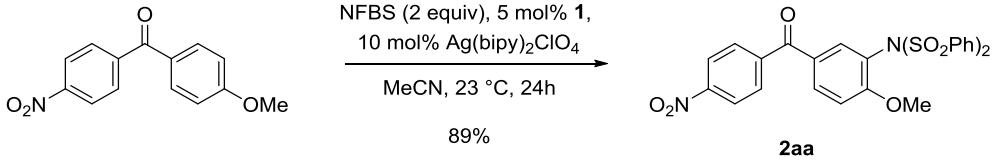



Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with (*E*)-4-methoxy-4-oxobut-2-en-1-yl 4-methoxybenzoate (75.1 mg, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0

µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (9:1 to 7:3 (v/v) with 1% triethylamine), to afford 132.7 mg of the title compound as an off-white solid (81% yield).

$R_f$ = 0.25 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 8.13 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 4H), 7.76 (d, *J* = 1.8 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.9 Hz, 4H), 7.02 (dt, *J* = 15.4, 4.6 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.05 (dt, *J* = 15.8, 1.8 Hz, 1H), 4.94 (dd, *J* = 4.7, 1.8 Hz, 2H), 3.78 (s, 3H), 3.47 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 166.3, 164.4, 161.7, 141.5, 139.9, 134.8, 134.1, 134.0, 128.9, 128.9, 123.1, 122.4, 122.0, 111.8, 63.1, 55.7, 51.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{25}H_{27}N_2O_9S_2$ ($[M+ NH_4]^+$), 563.1152, found, 563.1162.

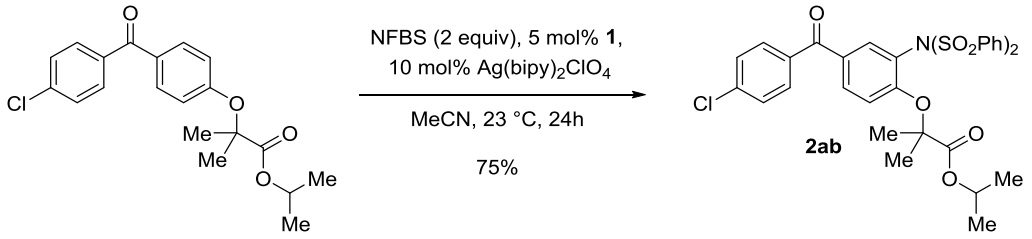
**_N_-(2-Methoxy-5-(4-nitrobenzoyl)phenyl)-_N_-(phenylsulfonyl)benzenesulfonamide (2aa)**




Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with (4-methoxyphenyl)(4-nitrophenyl)methanone (45.9 mg, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 3:2 (v/v) with 1% triethylamine), to afford 148 mg of the title compound as an off-white solid (89% yield).

$R_f$ = 0.47 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 8.33 (dt, *J* = 8.8, 1.8 Hz, 2H), 7.98 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.95 (dd, *J* = 7.6, 1.2 Hz, 4H), 7.87 (dt, *J* = 8.8, 2.3 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 1.8 Hz, 1H), 7.54 (t, *J* = 8.2 Hz, 4H), 6.97 (d, *J* = 8.2 Hz, 1H), 3.49 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 192.2, 161.9, 149.9, 142.9, 139.9, 135.8, 134.6, 134.1, 130.6, 129.1, 128.9, 128.9, 123.8, 123.2, 112.2, 55.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{26}H_{21}N_2O_8S_2$ ($[M + H]^+$), 553.0734, found, 553.0723.

**Isopropyl 2-(4-(4-chlorobenzoyl)-2-(*N*-(phenylsulfonyl)phenylsulfonamido)phenoxy)-2-methylpropanoate (2ab)**

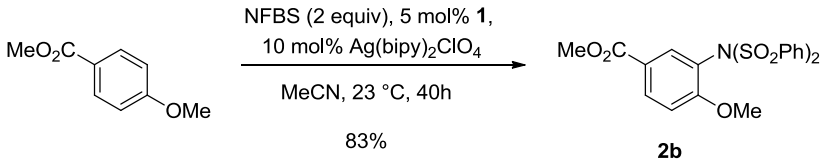



Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged Fenofibrate (isopropyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate) (108.2 mg, 0.300 mmol, 1.00 equiv), palladium complex **1** (11.4 mg, 15.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (16.0 mg, 30.0 µmol, 10.0 mol%), and NFBS (0.189 g, 0.600 mmol, 2.00 equiv). Acetonitrile (0.75 mL, c = 0.40 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, triethylamine (30.5 mg, 42.0 µL, 0.300 mmol, 1.00 equiv) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (19:1 to 5.7:1 (v/v) with 1% triethylamine), to afford 148.4 mg of the title compound as a colorless solid (75% yield).

$R_f$ = 0.57 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 8.01–8.04 (m, 4H), 7.86 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.68–7.70 (m, 2H), 7.64–7.68 (m, 2H), 7.56 (d, *J* = 2.3 Hz, 1H), 7.53–7.56 (m, 4H), 7.43–7.46 (m, 2H), 6.70 (d, *J* = 8.8 Hz, 1H), 5.07 (sep, *J* = 6.3 Hz, 1H), 1.34 (s, 6H), 1.25 (d, *J* = 6.5 Hz, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 192.8, 172.6, 158.0, 140.4, 138.9, 136.0, 135.7, 133.8, 133.1, 131.3, 129.8, 129.0, 129.0, 128.8, 124.4, 115.9, 80.5, 69.5, 24.3, 21.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{32}H_{34}ClN_2O_8S_2$ ($[M + NH_4]^+$), 673.144, found, 673.1455.

## Procedure for the multi-gram scale C–H imidation reaction

**Methyl 4-methoxy-3-(*N*-(phenylsulfonyl)phenylsulfonamido)benzoate (2b)**

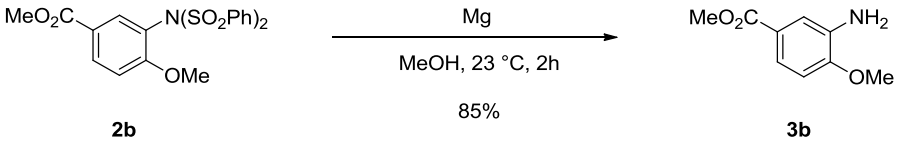



To a flame dried 250 mL round bottom flask charged with stir bar, *N*-fluoro-*N*-(phenylsulfonyl)benzenesulfonamide (14.2 g, 45.0 mmol, 1.50 equiv), palladium complex **1** (0.457 g, 0.600 mmol, 2.00 mol%), and $Ag(bipy)_2ClO_4$ (0.624 g, 1.20 mmol, 4.00 mol%) in dry MeCN (30.0 mL, c = 1.00 M) was added methyl 4-methoxybenzoate (4.99 g, 30.0 mmol, 1.00 equiv). The reaction vessel was sealed and stirred at 23 °C for 40 h. Triethylamine (5mL) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with (hexanes/EtOAc 5:1 (v/v) with 1% triethylamine) to

afford 11.5 g of the title compound (83% yield), which is spectroscopically identical to the compound prepared according to the standard procedure (*vide supra*).

## Procedure for removal of phenylsulfonyl groups

**Methyl 3-amino-4-methoxybenzoate (3b)**




**2b** **3b**

*0.108 mmol scale:*

To a solution of methyl 4-methoxy-3-(*N*-(phenylsulfonyl)phenylsulfonamido)benzoate (**2b**) (49.8 mg, 0.108 mmol, 1 equiv) in dry MeOH (3.6 mL, c = 0.030 M) was added Mg powder (31.6 mg, 1.30 mmol, 12 equiv) and the suspension was sonicated under nitrogen atmosphere at 23 °C for 2 h. Saturated solution of $NH_4Cl$ (2.0 mL) was then added and the resulting mixture was extracted with diethyl ether (3 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel, eluting with hexanes/EtOAc (5:1 (v/v) with 1% triethylamine) to afford 16.7 mg of the title compound as a yellow solid (85% yield).

$R_f$ = 0.70 ($CH_2Cl_2$/MeOH 9:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $(CD_3)_2SO$, 23 ºC, δ): 7.26 (d, *J* = 2.3 Hz, 1H), 7.21 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 4.97 (br s, 2H), 3.82 (s, 3H), 3.76 (s, 3 H). $^{13}$C NMR (125 MHz, $(CD_3)_2SO$, 23 ºC, δ): 166.5, 150.1, 137.7, 122.0, 118.3, 113.8, 109.8, 55.5, 51.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_9H_{12}NO_3$ ($[M + H]^+$), 182.0812, found, 182.0815.

*0.217 mmol scale:*

To a solution of methyl 4-methoxy-3-(*N*-(phenylsulfonyl)phenylsulfonamido)benzoate (**2b**) (100 mg, 0.217 mmol, 1 equiv) in dry MeOH (7.2 mL, c = 0.030 M) was added Mg powder (63.2 mg, 2.60 mmol, 12 equiv) and the suspension was sonicated under nitrogen atmosphere at 23 °C for 2 h. Saturated solution of $NH_4Cl$ (4.0 mL) was then added and the resulting mixture was extracted with diethyl ether (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel, eluting with hexanes/EtOAc (5:1 (v/v) with 1% triethylamine) to afford 29.0 mg of the title compound as a yellow solid (74% yield). Spectroscopic data are the same as described above.

## Control Experiments: Catalytic imidation in the absence of 1, $Ag(bipy)_2ClO_4$, and light

**Table S1. Experimental details**

| | Catalyst | Co-Catalyst | Light | NMR-Yield of |
|---|---|---|---|---|

| | (5 mol%) | (10 mol%) | | 2b |
|---|---|---|---|---|
| Standard | palladium complex **1** | $Ag(bipy)_2ClO_4$ | Yes | Quantitative |
| Absence of **1** | none | $Ag(bipy)_2ClO_4$ | Yes | < 10% |
| Absence of $Ag(bipy)_2ClO_4$ | palladium complex **1** | none | Yes | No Reaction |
| Absence of light | palladium complex **1** | $Ag(bipy)_2ClO_4$ | No | Quantitative |

**Standard:**

Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with methyl 4-methoxybenzoate (8.3 mg, 0.05 mmol, 1.0 equiv), palladium complex **1** (1.9 mg, 2.5 µmol, 5.0 mol%), $Ag(bipy)_2ClO_4$ (2.6 mg, 5.0 µmol, 10 mol%), and NFBS (32 mg, 0.10 mmol, 2.0 equiv). Acetonitrile (0.250 mL, c = 0.20 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, dimethylurea (2.2 mg, 0.025 mmol, 0.50 equiv) was added as an internal standard for the NMR measurement and the reaction mixture was concentrated *in vacuo*. The NMR of the crude reaction mixture indicated full conversation of starting material to the desired product **2b**.

**In the absence of 1:**

Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with methyl 4-methoxybenzoate (8.3 mg, 0.050 mmol, 1.0 equiv), $Ag(bipy)_2ClO_4$ (2.6 mg, 5.0 µmol, 10 mol%), and NFBS (32 mg, 0.10 mmol, 2.0 equiv). Acetonitrile (0.250 mL, c = 0.20 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, dimethylurea (2.2 mg, 0.025 mmol, 0.50 equiv) was added as an internal standard for the NMR measurement and the reaction mixture was concentrated *in vacuo*. The NMR of the crude reaction mixture indicated less than 10% conversation of starting material to the desired product **2b**.

**In the absence of $Ag(bipy)_2ClO_4$:**

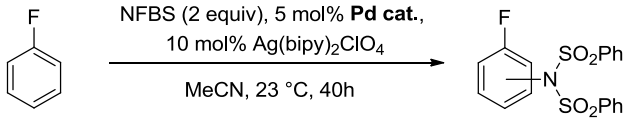
Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with methyl 4-methoxybenzoate (8.3 mg, 0.050 mmol, 1.0 equiv), palladium complex **1** (1.9 mg, 2.5 µmol, 5.0 mol%), and NFBS (32 mg, 0.10 mmol, 2.0 equiv). Acetonitrile (0.250 mL, c = 0.20 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, dimethylurea (2.2 mg, 0.025 mmol, 0.50 equiv) was added as an internal standard for the NMR measurement and the reaction mixture was concentrated *in vacuo*. The NMR of the crude reaction mixture indicated full conversation of starting material to the desired product **2b**.

**In the absence of light:**

Under $N_2$ atmosphere, an oven-dried amber 4 mL vial was charged with methyl 4-methoxybenzoate (8.3 mg, 0.050 mmol, 1.0 equiv), palladium complex **1** (1.9 mg, 2.5 µmol, 5.0 mol%), $Ag(bipy)_2ClO_4$ (2.6 mg, 5.0 µmol, 10 mol%), and NFBS (32 mg, 0.10 mmol,

2.0 equiv). The vial was wrapped with electrical tape and acetonitrile (0.250 mL, c = 0.20 M) was added. The reaction mixture was stirred in a sealed vial at 23 °C for 24 h. Subsequently, dimethylurea (2.2 mg, 0.025 mmol, 0.50 equiv) was added as an internal standard for the NMR measurement and the reaction mixture was concentrated *in vacuo*. The NMR of the crude reaction mixture indicated full conversation of starting material to the desired product **2b**.

## Control Experiments: Evaluation of Palladium Catalysts Other than 1




Under $N_2$ atmosphere, in a 4 mL vial was prepared a solution of NFBS (387.6 mg, 1.200 mmol, 2.0 equiv) and $Ag(bipy)_2ClO_4$ (31.2 mg, 0.0604 mmol, 10 mol%) in acetonitrile (3.00 mL). In 5 separate vials were weighed palladium source (0.0050 mmol, 5.0 mol%), and ligand (0.010 mmol, 10.0 mol%) if applicable (see Table S2 for details). To each of the five Pd/ligand-containing vials was added 0.500 mL of the NFBS/Ag solution. Finally, fluorobenzene (9.3 µL, 0.100 mmol, 1.0 equiv) was added to each vial. The five reactions were stirred magnetically at room temperature for 40 h, after which 2.0 uL 4-fluoronitrobenzene was added to each of the reaction mixtures as an internal standard and the product yields were analyzed by $^{19}F$ NMR (Table S2).

**Table S2. Experimental details**

| Reaction | Pd Catalyst | Vial Contents | Total yield of 2n |
|---|---|---|---|
| 1 | $Pd(OAc)_2$ | 1.1 mg $Pd(OAc)_2$ | > 1% |
| 2 | $Pd(NCMe)_4(OTf)_2$ | 2.8 mg $Pd(NCMe)_4(OTf)_2$ | 3% |
| 3 | $Pd(OAc)_2$ + 2 bathocuproine | 1.1 mg $Pd(OAc)_2$ 3.6 mg bathocuproine | > 1% |
| 4 | $Pd(NCMe)_4(OTf)_2$ + 2 bipyridine | 2.8 mg $Pd(NCMe)_4(OTf)_2$ 1.6 mg bipyridine | > 1% |
| 5 | $Pd(NCMe)_4(OTf)_2$ + 2 phenanthroline | 2.8 mg $Pd(NCMe)_4(OTf)_2$ 1.8 mg phenanthroline | 3% |

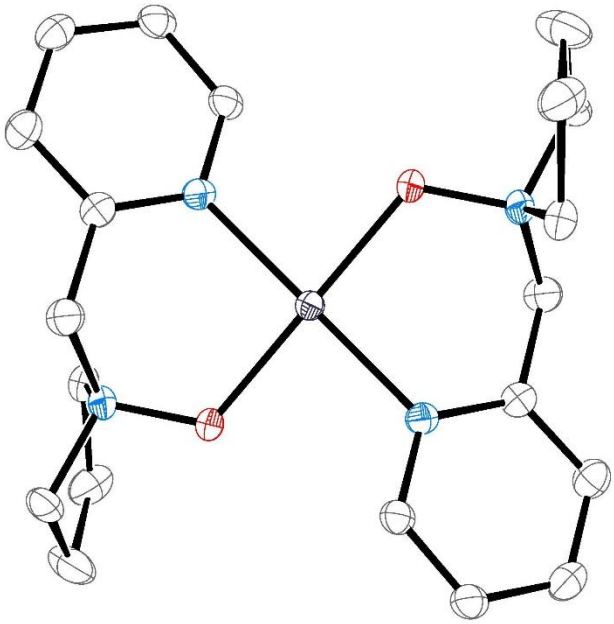
## X-ray Crystallographic Analysis

### Palladium complex 1 (CCDC 943631)

### Experimental

X-Ray quality crystals of **1** were grown by layering $Et_2O$ (ca. 0.2 mL) on top of a solution of ca. 5 mg of **1** in 0.2 mL MeCN A crystal was mounted on a nylon loop using Paratone-N oil, and

transferred to a Bruker APEX II CCD diffractometer (Mo$K\alpha$ radiation, $\lambda$=0.71073 Å) equipped with an Oxford Cryosystems nitrogen flow apparatus. The sample was held at 100 K during the experiment. The collection method involved 0.5° scans in $\omega$ at 28° in $2\theta$. Data integration down to 0.82 Å resolution was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimisation. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2009). The structure was solved by the direct methods procedure and refined by least-squares methods again $F^2$ using SHELXS-97 and SHELXL-97 (Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Restraints on bond lengths and constraints of the atomic displacement parameters on each pair of disorder fragments (SADI and EADP instructions of SHELXL97), as well as the restraints of the atomic displacement parameters (SIMU/DELU instructions of SHELXL97) if necessary, have been applied for the disorder refinement. Crystal data as well as details of data collection and refinement are summarized in Table 2.



X-ray structure of **1**. Thermal ellipsoids are drawn at the 50% probability level; triflate anions and hydrogen atoms omitted for clarity

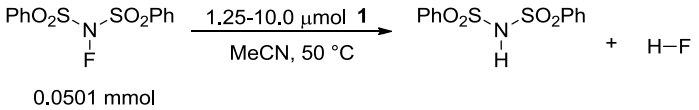
**Table 2. Experimental details**

| | Compound **1** |
|---|---|
| Crystal data | |
| Chemical formula | $C_{22}H_{28}F_6N_4O_8PdS_2$ |
| $M_r$ | 761.00 |
| Crystal system, space | Monoclinic, $P2_1/n$ |

| | |
|---|---|
| group | |
| Temperature (K) | 100 |
| *a*, *b*, *c* (Å) | 11.9987 (11), 8.0328 (8), 14.4450 (14) |
| β (°) | 96.490 (1) |
| *V* (Å$^3$) | 1383.3 (2) |
| *Z* | 2 |
| Radiation type | Mo *K*α |
| μ (mm$^{-1}$) | 0.92 |
| Crystal size (mm) | 0.40 × 0.30 × 0.20 |
| Data collection | |
| Diffractometer | CCD area detector diffractometer |
| Absorption correction | Multi-scan<br>*SADABS* (Sheldrick, 2009) |
| $T_{min}$, $T_{max}$ | 0.711, 0.838 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 22660, 3095, 2838 |
| $R_{int}$ | 0.033 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.644 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.044, 0.109, 1.04 |
| No. of reflections | 3095 |
| No. of parameters | 197 |
| No. of restraints | 13 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.23, -1.19 |

Computer programs: *APEX2* v2009.3.0 (Bruker-AXS, 2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

## Rate Law for NFBS Reduction Catalyzed by 1




This experiment was carried out under an $N_2$ atmosphere. A 0.167 M solution of NFBS in $CD_3CN$ was prepared in a vial and sealed with a septum cap. In five separate septum-sealed screw cap NMR tubes, solutions of **1** (1.25, 2.5, 3.75, 5.0, and 10 μmol) and 3-nitro-

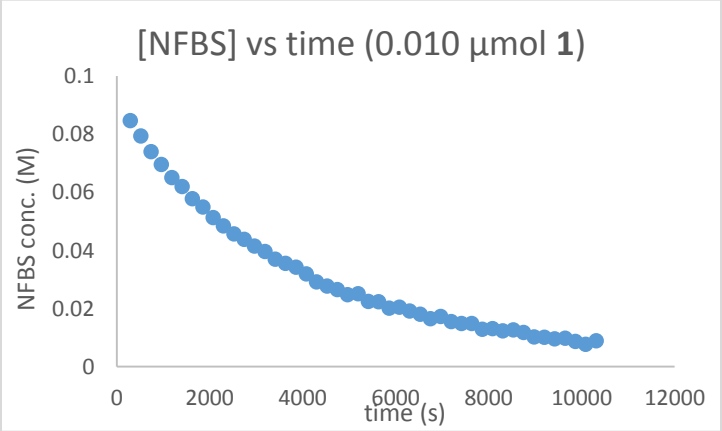
fluorobenzene (0.019–0.038 μmol) in 0.200 mL $CD_3CN$ were prepared in the following way:

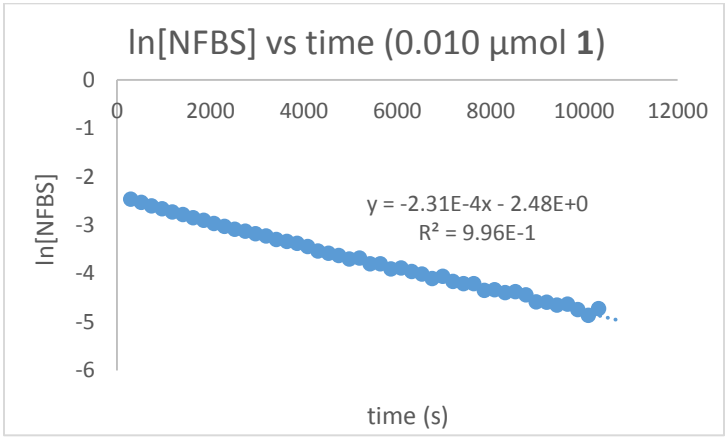
*1.25 and 2.50 μmol reactions:* A stock solution of 3.8 mg **1** (5.0 μmol) and 8.0 μL of 3-nitro-fluorobenzene (0.076 μmol) in 0.400 mL $CD_3CN$ was prepared. To one NMR tube (1.25 μmol **1**) was added 0.100 mL of the stock solution and 0.100 mL pure $CD_3CN$. To the other tube (2.5 μmol **1**) was added 0.200 mL of the stock solution.

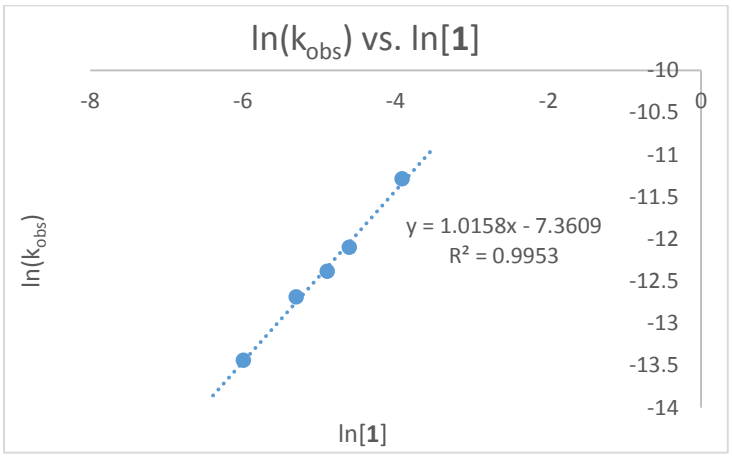
*3.75 and 5.0 μmol reactions:* A stock solution of 7.6 mg **1** (10 μmol) in 0.400 mL $CD_3CN$ was prepared. To one NMR tube (3.75 μmol **1**) was added 0.150 mL of the stock solution, 4.0 μL (0.038 μmol) 3-nitrofluorobenzene, and 0.050 mL pure $CD_3CN$. To the other tube (5.0 μmol **1**) was added 0.200 mL of the stock solution and 4.0 μL (0.038 μmol) 3-nitrofluorobenzene.

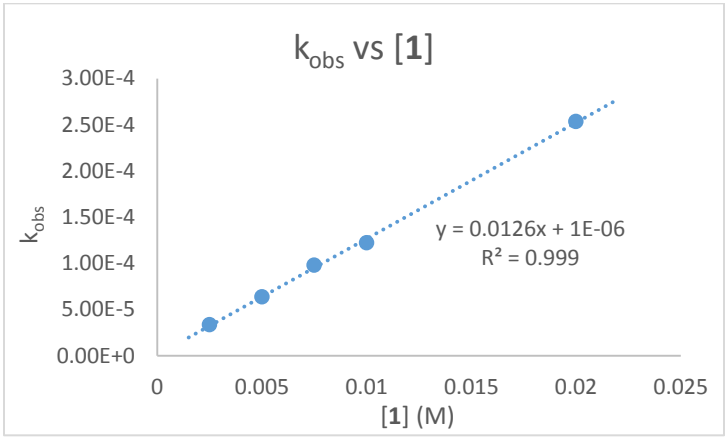
10 *μmol* reaction: A solution of 7.6 mg (10 μmol) **1** and and 4.0 μL (0.038 μmol) 3-nitrofluorobenzene in 0.200 mL $CD_3CN$ was prepared in an NMR tube.

For each reaction, 0.300 mL of the NFBS solution was added to the NMR tube via syringe, the sample was immediately inserted into the NMR probe pre-heated at 50 °C, and the consumption of NFBS was followed by integration of the $^{19}F$ NMR spectra with 3-nitro-fluorobenzene. The reactions were followed over 15-30% conversion, except the last one (10.0 μmol **1**), which was followed through 90% conversion (>3 half-lives). The plot of ln[NFBS] vs. time shows excellent linearity throughout, indicating an overall reaction order of unity. Pseudo-first-order analysis was therefore applied to determine the dependence of $k_{obs}$ on [**1**]. A plot of ln($k_{obs}$) vs ln[**1**] reveals a first order dependence on [**1**]. The overall rate law is therefore *rate* = $k$[**1**][NFBS]. A plot of $k_{obs}$ vs. [**1**] revealed a slope of $1.26\times10^{-2}$ $M^{-1}s^{-1}$, which is the value of $k$.





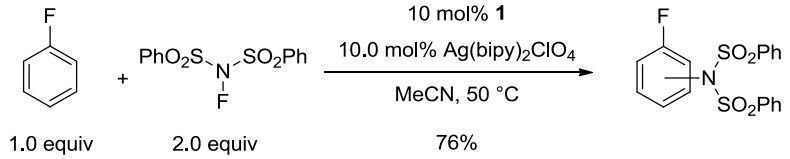




## Rate Law of Imidation Catalyzed by 1 and $Ag(bipy)_2ClO_4$

Fluorobenzene was chosen as the substrate for the determination of the rate law of the catalytic imidation reaction because fluorobenzene is a competent substrate for the imidation reaction (81% yield, Table 1), and the consumption of fluorobenzene and appearance of the products could be followed concurrently with the consumption of NFBS by $^{19}F$ NMR. The data was acquired at 50 °C because this temperature was found to facilitate a more convenient rate of reaction for

kinetic analysis. To justify the acquisition of kinetic data with fluorobenzene as a substrate at a reaction temperature of 50 °C, we have performed the catalytic imidation on fluorobenzene under these conditions, and found no substantial diminution in yield.

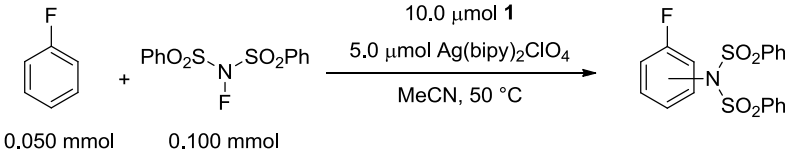
**Imidation of fluorobenzene at 50 °C**



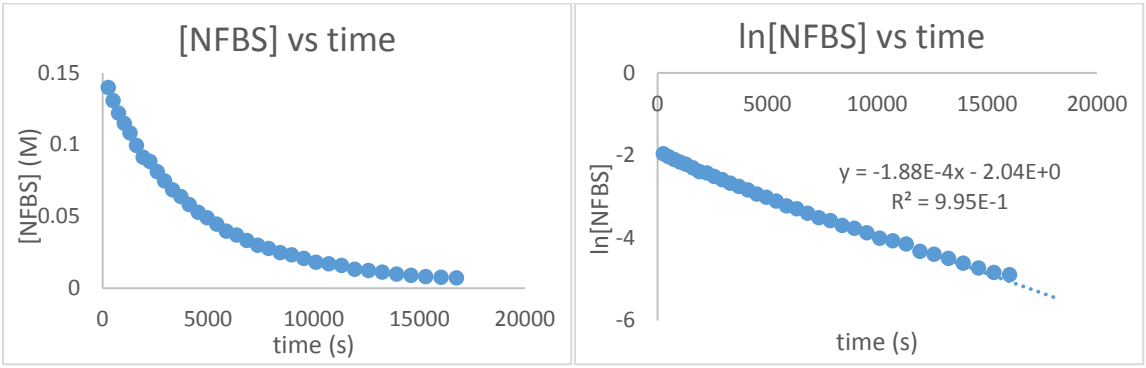

Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with fluorobenzene (9.3 µL, 0.10 mmol, 1.0 equiv), palladium complex **1** (7.6 mg, 10 µmol, 10 mol%), $Ag(bipy)_2ClO_4$ (5.2 mg, 10 µmol, 10 mol%), and NFBS (63.0 mg, 0.20 mmol, 2.0 equiv). Acetonitrile (0.500 mL, c = 0.20 M) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 12 h. Subsequently, 4-nitrofluorobenzene (2.0 µL, 0.0188 mmol) was added as an internal standard and the yield of the imidated products was measured by $^{19}F$ NMR.

| para (–108.7 ppm) | meta (–110.0 ppm) | ortho (–115.2 ppm) | Total |
|---|---|---|---|
| 30% | 12% | 34% | 76% |

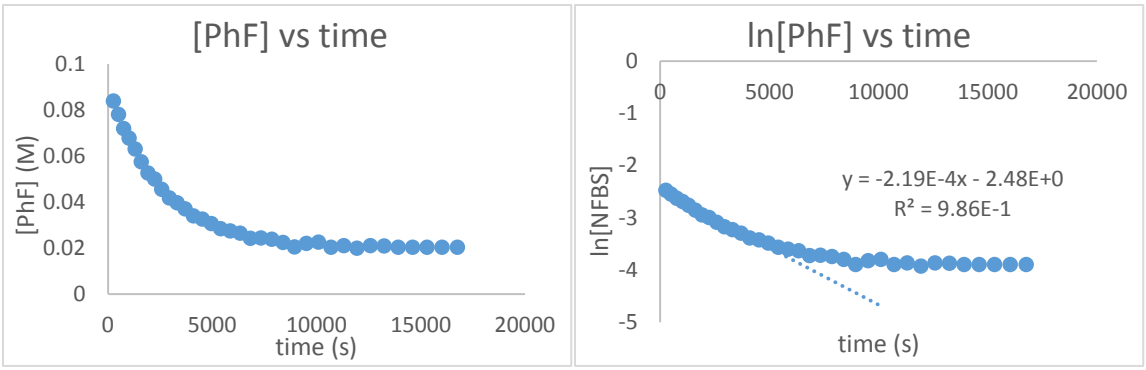
**Time course of the reaction**




This experiment was carried out under an $N_2$ atmosphere. A 0.333 M solution of NFBS in $CD_3CN$ was prepared in a vial and sealed with a septum cap. In a septum-sealed screw cap NMR tube was prepared a solution containing **1** (7.6 mg, 10 µmol), $Ag(bipy)_2ClO_4$ (2.6 mg, 5.0 µmol), fluorobenzene (4.7 µL, 0.050 mmol), and 3-nitro-fluorobenzene (2.0 µL, 0.019 µmol) in 0.200 mL $CD_3CN$. With a syringe, 0.300 mL of the NFBS solution was added to the NMR tube, the sample was immediately inserted into the NMR probe pre-heated to 50 °C, and the consumption of NFBS and fluorobenzene were followed over 4.5 h by measuring against 3-nitro-fluorobenzene by $^{19}F$ NMR. The consumption of NFBS follows clean first-order kinetics through ca. 95% conversion (>4 half-lifes).

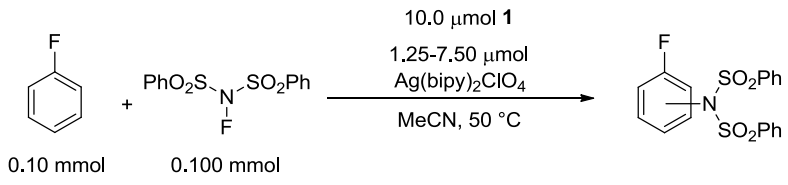



The consumption of fluorobenzene followed first-order kinetics only through ca. 70% conversion:



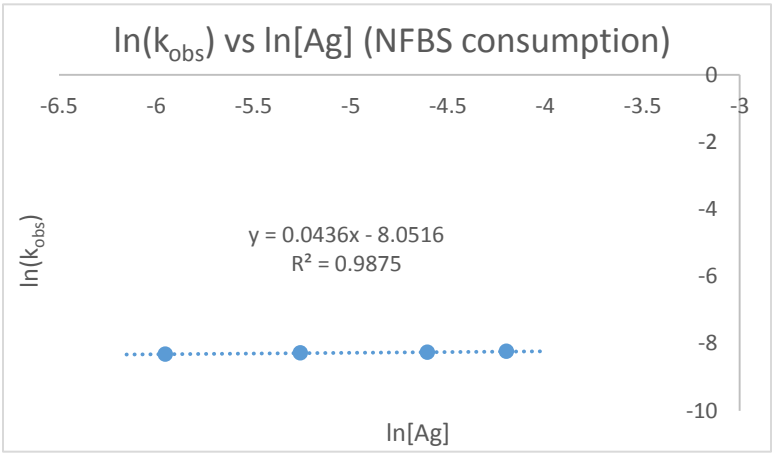

This observation can be explained considering the presence of a competitive, nonproductive NFBS reduction pathway. This nonproductive pathway causes NFBS to be expended before the arene substrate, which prematurely slows rate of fluorobenzene consumption. Since the consumption of fluorobenzene was followed only for the first ca. 20% for the purpose of rate law determination, pseudo first-order kinetic analysis is still appropriate.

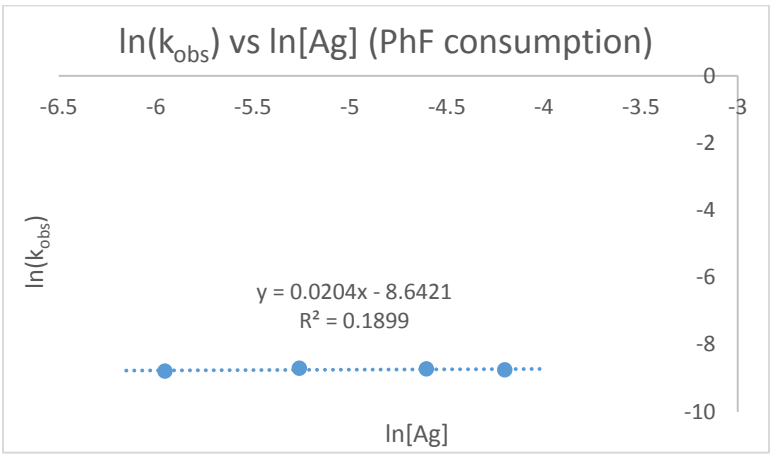
**Determination of order in $Ag(bipy)_2ClO_4$**




This experiment was carried out under an $N_2$ atmosphere. A 0.333 M solution of NFBS in $CD_3CN$ was prepared in a vial and sealed with a septum cap. In five separate septum-sealed screw cap NMR tubes, solutions containing **1** (10.0 μmol), $Ag(bipy)_2ClO_4$ (1.3, 2.6, 5.0, 7.5 μmol), fluorobenzene (0.10 mmol), and 3-nitro-fluorobenzene (0.019 mmol) in 0.200 mL $CD_3CN$ were prepared in the following way. A stock solution containing 22.8 mg **1** (0.030 mmol), 27.9 uL fluorobenzene (0.300 mmol), and 6.0 μL 3-nitrofluorobenzene (0.056 mmol) in $CD_3CN$ was prepared. Into four vials were weighed 0.8 mg, 1.6 mg, 3.1 mg, and 4.7 mg $Ag(bipy)_2ClO_4$,

respectively. The content of each vial was dissolved in 0.240 mL of the stock solution, and 0.200 mL of this mixture was transferred to an NMR tube. For each reaction, 0.300 mL of the NFBS solution was added to the NMR tube via syringe, the sample was immediately inserted into the NMR probe pre-heated to 50 °C, and the consumption of NFBS and fluorobenzene were followed by $^{19}F$ NMR, with 3-nitro-fluorobenzene as internal standard. The reactions were followed over ca. 20% conversion, and the results were subjected to pseudo first-order kinetic analysis.

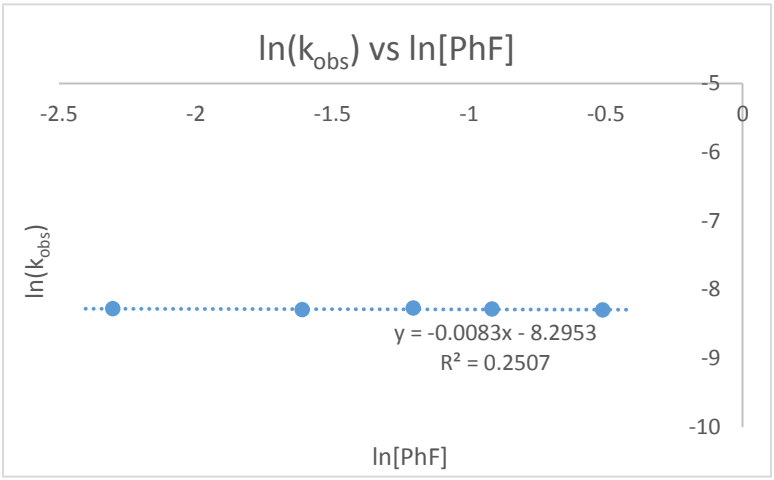


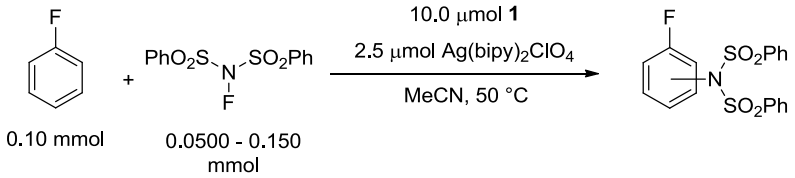

**Determination of order in arene substrate**


This experiment was carried out under an $N_2$ atmosphere. A 0.333 M solution of NFBS in $CD_3CN$ was prepared in a vial and sealed with a septum cap. In five separate septum-sealed screw cap NMR tubes were prepared solutions containing **1** (7.6 mg, 10 μmol), $Ag(bipy)_2ClO_4$ (1.3 mg, 2.5 μmol), and 3-nitro-fluorobenzene (2.0 μL, 0.019 μmol) in 0.200 mL $CD_3CN$. To

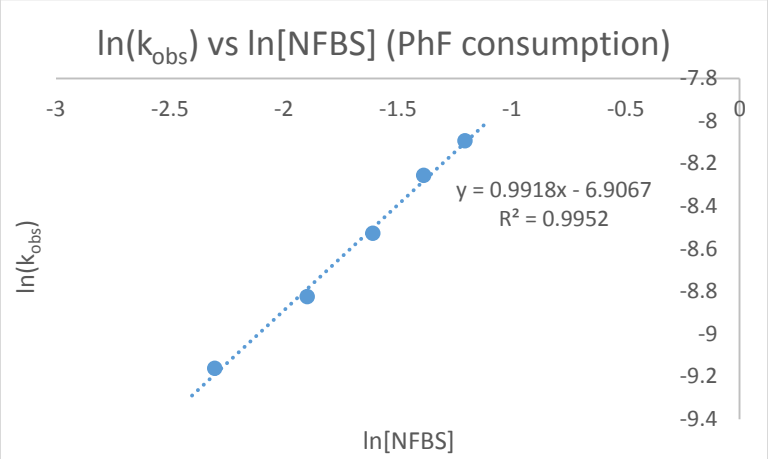
each tube was then added 4.7, 9.4, 14.1, 18.8, and 27.9 µL fluorobenzene (0.050, 0.10, 0.150, 0.200, and 0.300 mmol, respectively). For each reaction, 0.300 mL of the NFBS solution was added to the NMR tube via syringe, the sample was immediately inserted into the NMR probe pre-heated to 50 °C, and the consumption of NFBS was followed by $^{19}$F NMR, with 3-nitro-fluorobenzene as internal standard. The reactions were followed over ca. 20% conversion, and the results were subjected to pseudo first-order kinetic analysis.



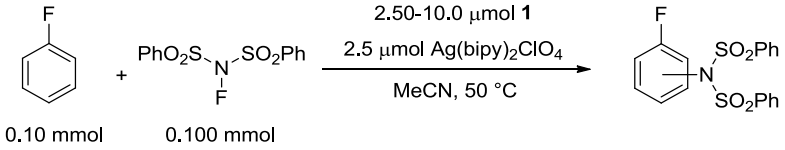

**Determination of order in NFBS**




This experiment was carried out under an $N_2$ atmosphere. A solution of NFBS (0.500 M) in $CD_3CN$ was prepared in a vial and sealed with a septum cap. In five separate septum-sealed screw cap NMR tubes were prepared solutions containing **1** (7.6 mg, 10.0 µmol), $Ag(bipy)_2ClO_4$ (1.3 mg, 2.5 µmol), fluorobenzene (9.3 µL, 0.10 mmol), and 3-nitro-fluorobenzene (2.0 µL, 0.019 µmol) in the volume of $CD_3CN$ which would make 0.500 mL after addition of the NFBS solution (see below). The NFBS solution was added to the NMR tube via syringe (0.10 mL, 0.15 mL, 0.20 mL, 0.25 mL, and 0.30 mL). The sample was immediately inserted into the NMR probe pre-heated to 50 °C, and the consumption of fluorobenzene was followed by $^{19}$F NMR, with 3-nitro-fluorobenzene as internal standard. The reactions were followed over ca. 20% conversion, and the results were subjected to pseudo first-order kinetic analysis.




**Determination of order in 1**



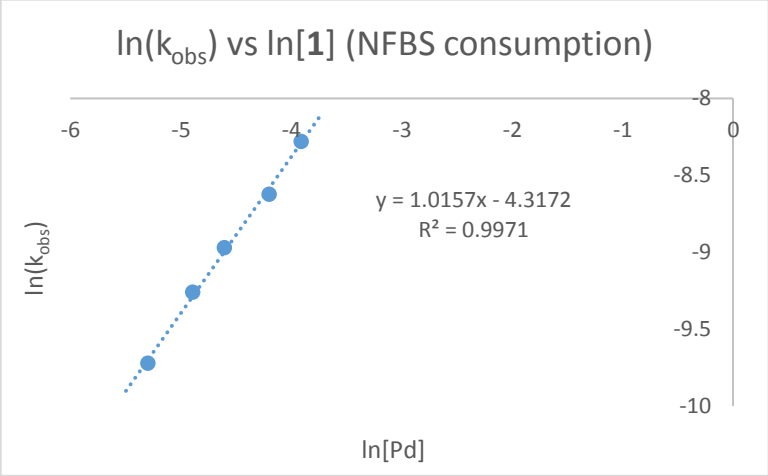

This experiment was carried out under an $N_2$ atmosphere. A 0.333 M solution of NFBS in $CD_3CN$ was prepared in a vial and sealed with a septum cap. In five separate septum-sealed screw cap NMR tubes, solutions containing **1** (2.50, 3.75, 5.00, 7.50, and 10.0 μmol), $Ag(bipy)_2ClO_4$ (1.3 mg, 2.5 μmol), fluorobenzene (9.3 μL, 0.10 mmol), and 3-nitro-fluorobenzene (2.0 μL, 0.019 μmol) in 0.200 mL $CD_3CN$ were prepared in the following way:

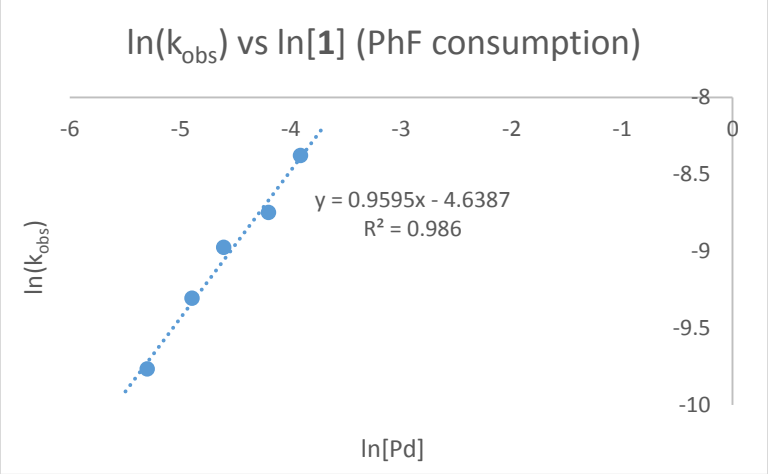
*3.75 and 7.5 μmol **1**:* Two stock solutions were prepared. Solution A contained 11.4 mg **1** (0.0150 mmol) in $CD_3CN$, and Solution B contained 5.2 mg $Ag(bipy)_2ClO_4$ (0.010 mmol), 37.2 μL fluorobenzene (0.400 mmol), and 8.0 μL 3-nitrofluorobenzene (0.075 mmol) in 0.200 mL $CD_3CN$. To one NMR tube (3.75 μmol **1**) were added 0.075 mL Solution A, 0.050 mL Solution B, and 0.075 mL pure CD3CN. To another NMR tube (7.5 μmol **1**) were added 0.150 mL Solution A and 0.050 mL Solution B.

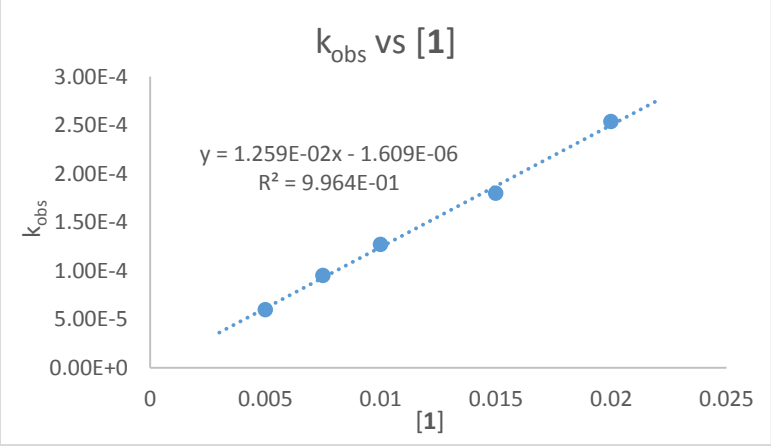
*2.5 and 5.0 μmol **1**:* Two stock solutions were prepared. Solution A contained 7.6 mg **1** (0.015 mmol) in $CD_3CN$, and Solution B contained 5.2 mg $Ag(bipy)_2ClO_4$ (0.010 mmol), 37.2 μL fluorobenzene (0.400 mmol), and 8.0 μL 3-nitrofluorobenzene (0.075 mmol) in 0.200 mL $CD_3CN$. To one NMR tube (2.5 μmol **1**) were added 0.075 mL Solution A, 0.050 mL Solution B, and 0.075 mL pure CD3CN. To another NMR tube (5.0 μmol **1**) were added 0.150 mL Solution A and 0.050 mL Solution B.

*10 μmol **1**:* Two stock solutions were prepared. Solution A contained 15.2 mg **1** (0.020 mmol) in $CD_3CN$, and Solution B contained 5.2 mg $Ag(bipy)_2ClO_4$ (0.010 mmol), 37.2 μL fluorobenzene (0.400 mmol), and 8.0 μL 3-nitrofluorobenzene (0.076 mmol) in 0.200 mL $CD_3CN$. To an NMR tube was added 0.150 mL Solution A and 0.050 mL Solution B.

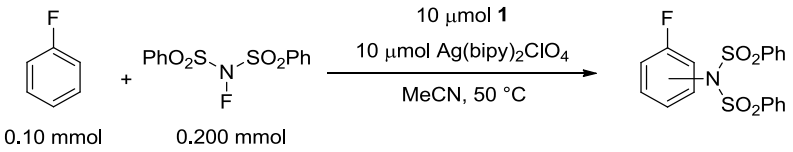
For each reaction, 0.300 mL of the NFBS solution was added to the NMR tube via syringe, the sample was immediately inserted into the NMR probe pre-heated to 50 °C, and the consumption of NFBS and fluorobenzene were followed by by $^{19}F$ NMR, with 3-nitro-fluorobenzene as internal standard. The reactions were followed over ca. 20% conversion, and the results were subjected to pseudo first-order kinetic analysis.



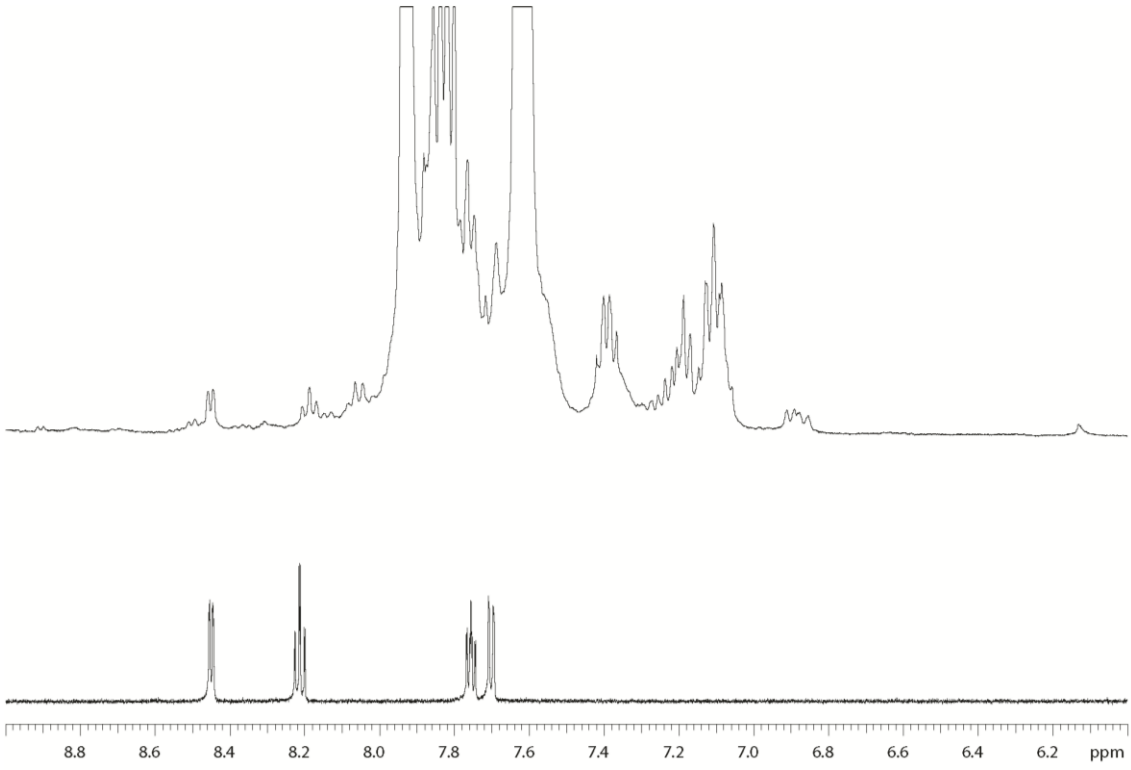



## Determination of the Resting State

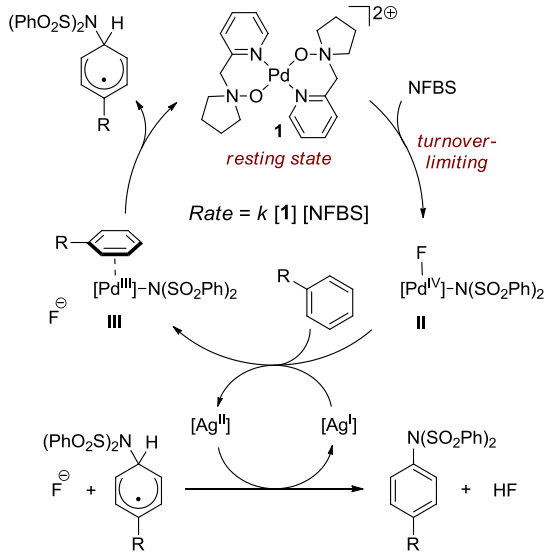



Under an $N_2$ atmosphere, into a vial (A) a solution of **1** (15.6 mg, 0.204 mmol) and 1,2-dichloroethane (8.0 μL, 0.10 mmol) in $CD_3CN$ (1.000 mL) was prepared. In a separate vial (B) were weighed NFBS (63.0 mg, 0.200 mmol, 2.00 equiv) and $Ag(bipy)_2ClO_4$ (5.2 mg, 0.010 mmol, 10 mol%). The contents of vial B were dissolved in half of the solution in vial A (0.500 mL), and fluorobenzene (9.3 μL, 0.10 mmol) was added to vial B. The contents of each vial was transferred to an NMR tube. The solution from vial A (containing only **1** and 1,2-dichloroethane) was analyzed by $^1H$ NMR, and the actual ratio of complex **1**:1,2-dichloroethane was measured to be 0.22:1. The solution from vial B (catalytic imidation reaction) was inserted into an NMR probe pre-heated to 50 °C. After 12 minutes, the conversion was measured to be ca. 31% by $^{19}F$ NMR. A $^1H$ NMR of the reaction mixture was also recorded, and the actual ratio of complex 1:1,2-dichloroethane was measured to be 0.15:1. Complex **1** was therefore found to account for 67% of the palladium-containing species. We attribute the diminution in the amount of **1** to decomposition during catalysis.




*In-situ* $^1H$ NMR of catalytic imidation (top), and pure **1** (bottom)

## Role of the co-catalyst




**Scheme 1:** Mechanistic hypothesis

The co-catalyst is proposed to be responsible for the reduction of intermediate **II** in order to generate intermediate **III**, the actual C–N bond forming species. Evidence supporting this proposal is outlined below.

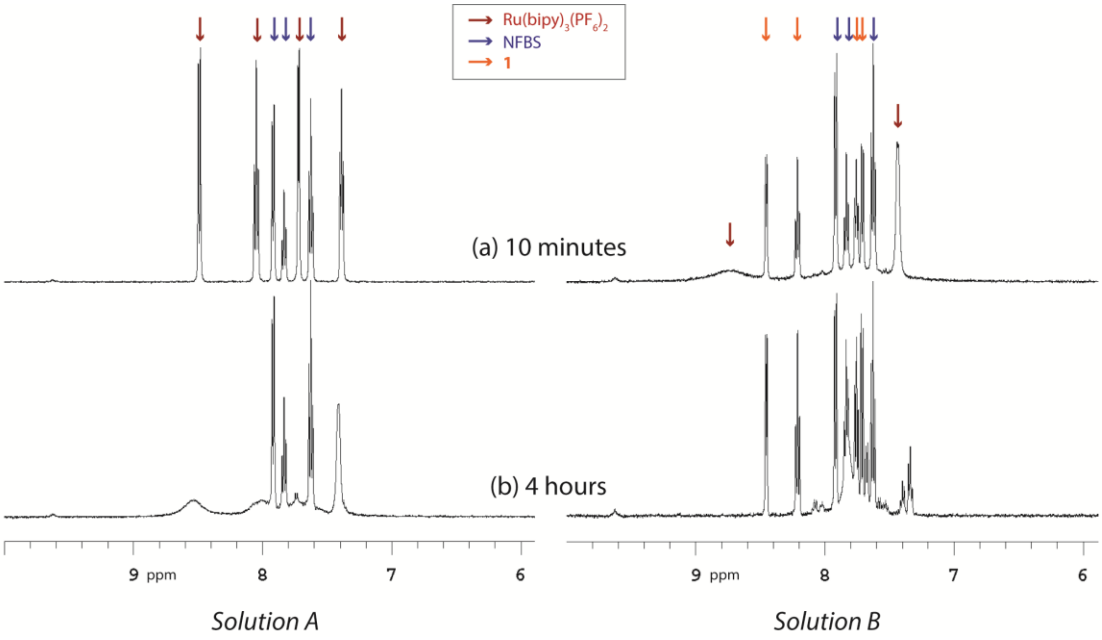
### Oxidation of $Ru(bipy)_3(PF_6)_2$ mediated by 1

$$Ru(bipy)_3(PF_6)_2 \xrightarrow[MeCN,\ 23\ °C]{1\ \text{equiv NFBS}} Ru(bipy)_3^{3+}$$

$$Ru(bipy)_3(PF_6)_2 \xrightarrow[MeCN,\ 23\ °C]{1\ \text{equiv } \mathbf{1}\ ;\ 1\ \text{equiv NFBS}} Ru(bipy)_3^{3+}$$

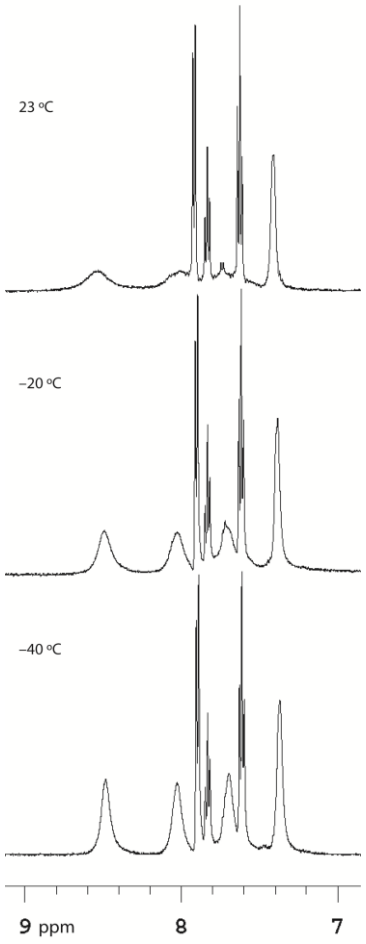
Under an $N_2$ atmosphere, two solutions were prepared in NMR tubes: Solution A contained $Ru(bipy)_3(PF_6)_2$ (5.0 mg, 5.8 μmol) and NFBS (1.8 mg, 5.7 μmol) in $CD_3CN$ (0.80 mL), and Solution B contained **1** (4.4 mg, 5.8 μmol), $Ru(bipy)_3(PF_6)_2$ (5.0 mg, 5.8 μmol) and NFBS (1.8 mg, 5.7 μmol) in $CD_3CN$ (0.80 mL). After 10 minutes, each solution was analyzed by $^1H$ NMR (Figure S1a). The spectrum of Solution A showed sharp signals for $Ru(bipy)_3(PF_6)_2$ and NFBS, while Solution B showed sharp signals for **1** and NFBS, but dramatically broadened signals for $Ru(bipy)_3(PF_6)_2$. After standing for 4 hours at room temperature, the solutions were analyzed again by $^1H$ and $^{19}F$ NMR (Figure S1b). The $^1H$ NMR spectrum of Solution A showed sharp signals for NFBS but broadened signals for $Ru(bipy)_2(PF_6)_2$, and the $^{19}F$ NMR of Solution A showed only 9 % NFBS consumption. The $^1H$ NMR spectrum of Solution B showed no sign of $Ru(bipy)_3(PF_6)_2$ (Figure S2b), and the $^{19}F$ NMR of solution B showed 61% NFBS conversion.

**Figure S1. $^{1}$H NMR spectra of Solution A (left) and Solution B (right) after 10 minutes (a, top) and 4 hours (b, bottom)**




The broadening of the signals due to $Ru(bipy)_3^{2+}$ is attributed to partial oxidation to $Ru(bipy)_3^{3+}$, with rapid redox exchange between the Ru(II) and Ru(III) species causing the broadening. This interpretation is supported by low temperature NMR of Solution A after 4 hours of standing at room temperature, which shows the peaks due to $Ru(bipy)_3^{2+}$ sharpening as temperature decreases, consistent with slower exchange at lower temperature (Figure S2).

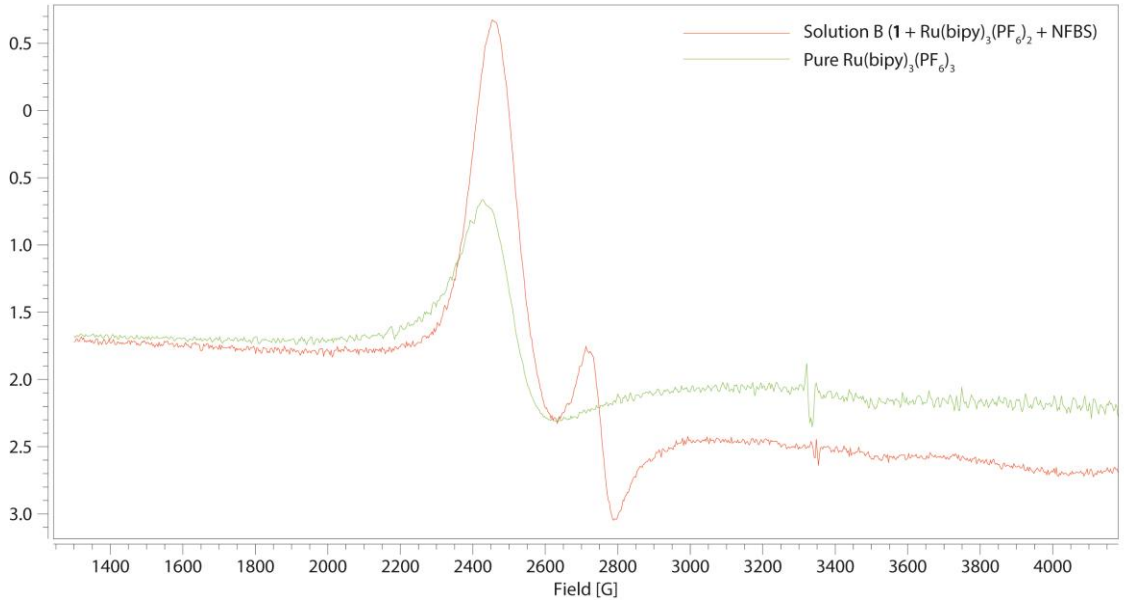
**Figure S2. $^{1}$H NMR peak broadness at 23 °C, –20 °C, and –40 °C**




EPR spectroscopy provides evidence for the formation of $Ru(bipy)_3^{3+}$ in Solution B. After 5 hours, Solution B was transferred to an EPR tube and frozen in liquid nitrogen. The resulting glass was analyzed by EPR spectroscopy along with a sample containing pure $Ru(bipy)_3(PF_6)_3$, prepared according to a literature procedure.[4] The EPR spectrum of Solution B (Figure S3) shows a paramagnetic resonance assignable to $Ru(bipy)_3^{3+}$, along with a partially overlapping second resonance (possibly a Pd(III) species generated upon oxidation of $Ru(bipy)_3^{2+}$).

[4] Biner, M.; Buergi, H. B.; Ludi, A.; Roehr, C. *J. Am. Chem. Soc.* **1992**, *114*, 5197-5203.

**Figure S3. EPR spectra of Solution B and pure $Ru(bipy)_3(PF_6)_3$**

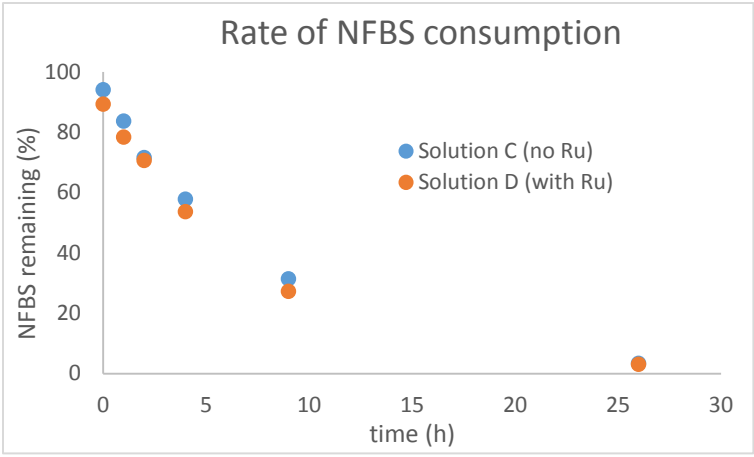



The data shown in Figures S1–S3 combined demonstrate an acceleration of the oxidation of $Ru(bipy)_2^{2+}$ to $Ru(bipy)_2^{3+}$ in the presence of **1**.

**Comparison of rates of NFBS reduction by 1, and 1 + $Ru(bipy)_3(PF_6)_2$**

Under an $N_2$ atmosphere, two solutions were prepared in NMR tubes: Solution C contained **1** (4.4 mg, 5.8 µmol) and NFBS (1.8 mg, 5.7 µmol) in $CD_3CN$ (0.60 mL), and Solution D contained **1** (4.4 mg, 5.8 µmol), $Ru(bipy)_3(PF_6)_2$ (5.0 mg, 5.8 µmol) and NFBS (1.8 mg, 5.7 µmol) in $CD_3CN$ (0.60 mL). The consumption of NFBS in both solutions was followed by $^{19}F$ NMR over 26 hours, and the rates were found to be identical (Figure S4).

**Figure S4. Rates of NFBS consumption by $Ru(bipy)_3(PF_6)_2$ vs. by 1 + $Ru(bipy)_3(PF_6)_2$**



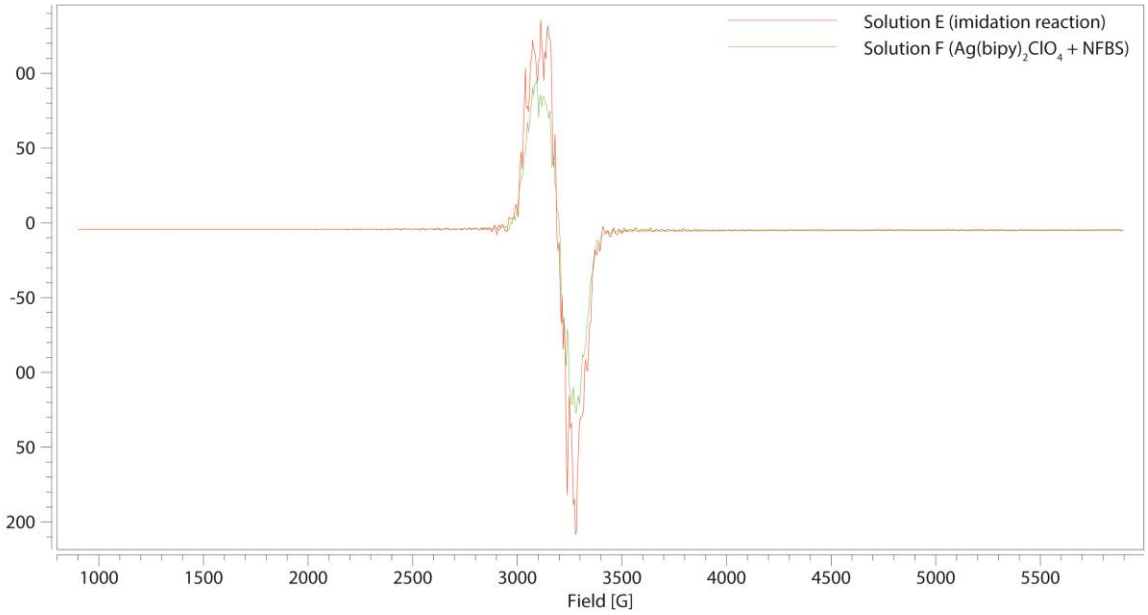
**Discussion**

The above data indicate the following: (1) NFBS reacts with palladium catalyst **1** more rapidly than with $Ru(bipy)_3^{2+}$, (2) $Ru(bipy)_3^{3+}$ forms much more rapidly in the presence of **1** and NFBS than with NFBS alone, (3) the rate of NFBS oxidation of $Ru(bipy)_3^{2+}$ mediated by **1** is limited by the rate of oxidation of **1** by NFBS. These observations combined are consistent with a scenario in which palladium catalyst **1** is oxidized by NFBS to give the putative high-valent intermediate **II**, followed by single electron oxidation of $Ru(bipy)_3^{2+}$ by **II** to yield $Ru(bipy)_3^{3+}$ and a Pd(III) intermediate (possibly a progenitor to **III** in Scheme 1).

**Observation of $Ag^{II}(bipy)_2$ in the catalytic imidation reaction**

Under an $N_2$ atmosphere, two solutions were prepared. Solution E contained **1** (3.8 mg, 5.0 μmol), $Ag(bipy)_2ClO_4$ (5.2 mg, 10 μmol), NFBS (63.1 mg, 0.200 mmol), and fluorobenzene (9.4 μL, 0.10 mmol) in 0.50 mL MeCN. Solution F contained $Ag(bipy)_2ClO_4$ (5.2 mg, 10 μmol) and NFBS (63.1 mg, 0.200 mmol) in 0.50 mL MeCN. Both solutions were transferred to EPR tubes and were frozen in liquid nitrogen after 1 hour, and the resulting glasses were analyzed by EPR spectroscopy (Figure S5). Both spectra show the same signal, assigned to an $Ag(bipy)_2^{2+}$ species.

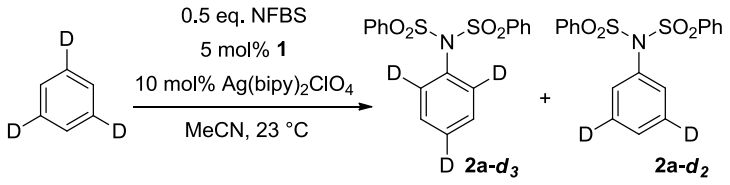
**Figure S5. EPR spectra of Solutions E and F.**




The above data demonstrates that an $Ag(bipy)_2^{2+}$ species is present in the catalytic imidation reaction mixture.

# Competition Kinetic Isotope Effect Experiments

### Intramolecular Competition KIE Experiment




Under $N_2$ atmosphere, an oven-dried 4 mL vial was charged with 1,3,5-trideuterobenzene (89.2 µL, 1.00 mmol, 2.00 equiv), palladium complex **1** (19.0 mg, 25.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (25.8 mg, 50.0 µmol, 10.0 mol%), and NFBS (0.158 g, 0.500 mmol, 1.00 equiv). Acetonitrile (1.25 mL) was added and the reaction mixture was stirred in a sealed vial at 23 °C for 29 h. Subsequently, triethylamine (200 µL) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (4:1 (v/v)), to afford 118.0 mg of the title compound as a colorless solid (0.314 mmol, 63% yield based on NFBS).

$R_f$ = 0.51 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.95 (dd, *J* = 8.8, 1.2 Hz, 4H), 7.66–7.69 (m, 2H), 7.53–7.57 (m, 4H), 7.44–7.47 (m, 0.57H), 7.34–7.38 (m, 1.01H), 7.02–7.05 (m, 1.11H).

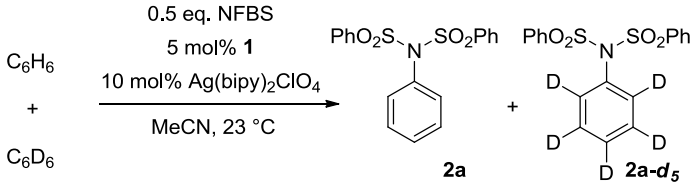
*Ratio of **2a-$d_3$/2a-$d_2$**, measured by $^1$H NMR:* the $^1$H NMR spectrum was recorded nine times with seven minutes between spectra to assure full relaxation. The peak at 7.03 ppm (the 2- and 6-positions in **2a-$d_2$**) were integrated against the peak at 7.95 ppm (the 2- and 6- positions in the sulphonyl phenyl groups, set to 4.0H) in each spectrum. The average of these measurements yielded **2a-$d_3$/2a-$d_2$** = 0.80, with a standard deviation of 0.0056 (95% confidence interval: ± 0.011).

*Ratio of **2a-$d_3$/2a-$d_2$**, measured by mass spectrometry:* the mixture was analyzed three times by GC/MS (EI detector) in single ion mode, counting $M^{+\bullet}$ at m/z = 375 and 376. Because the peak at m/z=376 has a contribution from both **2a-$d_3$** and (M+1) for **2a-$d_2$** (natural abundance: 19.5%), the following formula was necessary to extract the ratio of **2a-$d_3$/2a-$d_2$**:

$$\frac{k_H}{k_D} = \frac{[\mathbf{2a\text{-}d_3}]}{[\mathbf{2a\text{-}d_2}]} = \frac{A_{376} - 0.195 \times A_{375}}{A_{375}}$$

Where $A_{376}$ and $A_{375}$ are the areas for the peaks at m/z = 376 and 375, respectively. Through this treatment, the three measurements yielded **2a-$d_3$/2a-$d_2$** = 0.80 (average), with a standard deviation of 0.017 (95% confidence interval: ± 0.034).

**Intermolecular Competition KIE Experiment**




**Intermolecular KIE: 2a/2a-$d_5$** = 1.03 ± 0.02

Under $N_2$ atmosphere, an oven-dried 4 mL vial (A) was charged with palladium complex **1** (19.0 mg, 25.0 µmol, 5.00 mol%), $Ag(bipy)_2ClO_4$ (25.8 mg, 50.0 µmol, 10.0 mol%), and NFBS (0.158 g, 0.500 mmol, 1.00 equiv). In a separate vial (B), a solution of $C_6H_6$ (90.2 µL, 1.00 mmol) and $C_6D_6$ (88.6 µL, 1.00 mmol) was prepared in 2.50 mL acetonitrile. The contents of vial A were dissolved in 1.25 mL of the solution in vial B, and the reaction mixture was stirred in the sealed vial at 23 °C for 8 h. Subsequently, triethylamine (200 µL) was added and the reaction mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (4:1 (v/v)), to afford 73.3 mg of the title compound as a colorless solid (0.195 mmol, 39% yield based on NFBS). The remainder of the solution in vial B was subjected to GC/MS analysis, and the actual ratio of $C_6H_6$ to $C_6D_6$ was measured.

$R_f$ = 0.51 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.95 (dd, *J* = 8.8, 1.2 Hz, 4H), 7.66–7.69 (m, 2H), 7.53–7.57 (m, 4H), 7.44–7.47 (m, 0.53H), 7.34–7.38 (m, 1.04H), 7.02–7.05 (m, 1.04H).

*Ratio of **2a**/**2a-$d_5$**, measured by $^1$H NMR:* the $^1$H NMR spectrum was recorded nine times with seven minutes between spectra to assure full relaxation. The peak at 7.03 ppm (the 2- and 6-positions in **2a**) were integrated against the peak at 7.95 ppm (the 2- and 6- positions in the sulphonyl phenyl groups, set to 4.0H) in each spectrum. The average of these measurements, correcting for the measured actual starting ratio of $C_6H_6$ to $C_6D_6$, yielded **2a**/**2a-$d_5$** = 1.03, with a standard deviation of 0.010 (95% confidence interval: ± 0.020).

*Ratio of **2a**/**2a-$d_5$**, measured by mass spectrometry:* the mixture was analyzed three times by GC/MS (EI detector) in single ion mode, counting $M^{+\bullet}$ at m/z = 373 and 378. Division of the areas of the resulting peaks yielded **2a**/**2a-$d_5$** = 1.03, with a standard deviation of 0.0038 (95% confidence interval: ± 0.076). Correcting for the measured actual starting ratio of $C_6H_6$ to $C_6D_6$, this corresponds to $k_H/k_D$ = 0.99 ± 0.076.

## DFT Calculations

Density functional theory (DFT) calculations were performed using Gaussian09[5] on the Odyssey

[5] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; , J.

cluster at Harvard University. Geometry optimization was carried out using the atomic coordinates from the crystal structure of **1** as a starting point. BS I includes SDD quasirelativistic pseudopotentials on Pd (MWB28) with basis sets (Pd: (8s7p6d)/[6s5p3d] [6] ) extended by polarization functions (Pd: f, 1.472[7]) and 6-31G(d,p)[8] on H, C, N. All geometry optimizations were performed using the B3PW91 functional with the BS I basis set. Molecular orbitals were generated using an isosurface value of 0.03 with B3PW91/BS I. Images were generated using Chem3D.[9]

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A. Montgomery, J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd; J. J. Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Normand; J. Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Cossi, J. M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adam, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels; A. D. Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski; J. Fox, D. J. *Gaussian 09, Revision A.02*; Gaussian, Inc.: Wallingford CT, 2009.

[6] (a) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123-141. (b) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1991**, *78*, 247-266.

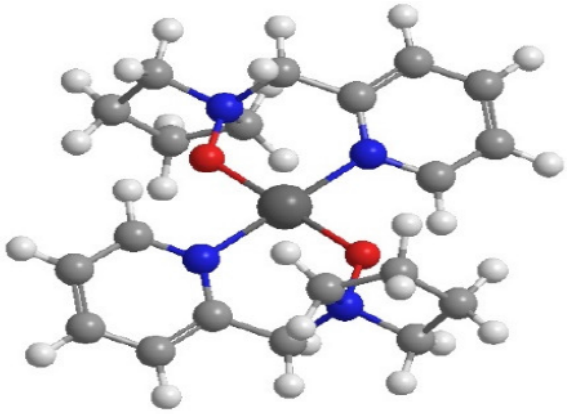
[7] Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett*. **1993**, *208*, 111-114.

[8] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213-222.

[9] Dennington, R., II; Keith, T. A.; Millam, J. M. *GaussView*, Version 5.0.8; Semichem, Inc.

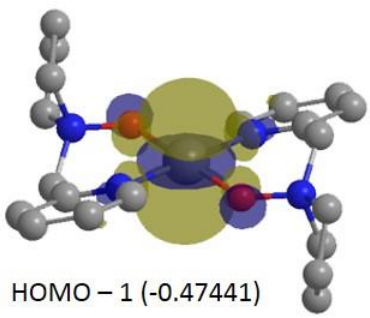
**Optimized structure of 1 with B3PW91 and Cartesian Coordinates**

| Atom | X | Y | Z |
|---|---|---|---|
| Pd | 5.999378 | 0.000108 | 0.000129 |
| O | 7.943265 | 0.526134 | 0.062967 |
| N | 6.342291 | -1.852816 | 0.827158 |
| N | 8.91326 | -0.358592 | 0.527153 |
| C | 5.344906 | -2.479767 | 1.476335 |
| H | 4.399548 | -1.951777 | 1.504105 |
| C | 8.659543 | -1.744523 | 0.015094 |
| H | 9.584661 | -2.314277 | 0.119394 |
| H | 8.436598 | -1.62791 | -1.049754 |
| C | 5.504448 | -3.733043 | 2.053905 |
| H | 4.668135 | -4.195557 | 2.566382 |
| C | 10.23979 | 0.190486 | 0.037144 |
| H | 10.984836 | -0.592736 | 0.203955 |
| H | 10.144756 | 0.386886 | -1.030801 |
| C | 7.552038 | -2.45029 | 0.744641 |
| C | 6.738743 | -4.363119 | 1.961056 |
| H | 6.899983 | -5.343865 | 2.397368 |
| C | 9.03959 | -0.244825 | 2.030555 |
| H | 9.637431 | -1.098483 | 2.364786 |
| H | 8.039567 | -0.310526 | 2.458308 |
| C | 7.774736 | -3.70504 | 1.301551 |
| H | 8.753386 | -4.165735 | 1.214057 |
| C | 9.750721 | 1.091741 | 2.252214 |
| H | 10.440573 | 1.010404 | 3.094488 |
| H | 9.031599 | 1.876081 | 2.491626 |
| C | 10.482564 | 1.40646 | 0.922526 |
| H | 10.075292 | 2.306766 | 0.461018 |
| H | 11.554128 | 1.561904 | 1.06216 |
| O | 4.055564 | -0.526119 | -0.062922 |
| N | 5.656352 | 1.853038 | -0.826886 |
| N | 3.085538 | 0.35851 | -0.527216 |
| C | 6.6537 | 2.480106 | -1.47601 |
| C | 3.339029 | 1.744447 | -0.015062 |
| C | 6.49406 | 3.733385 | -2.05355 |
| C | 1.759016 | -0.190761 | -0.037405 |
| C | 4.446532 | 2.450378 | -0.744452 |

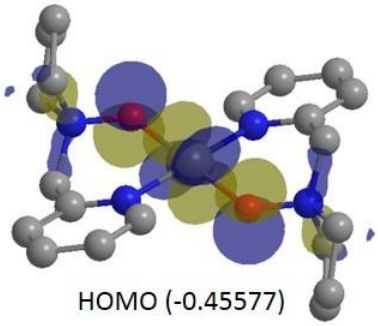


| Atom | X | Y | Z |
|---|---|---|---|
| C | 5.259697 | 4.363332 | -1.960754 |
| C | 2.95942 | 0.244798 | -2.030643 |
| C | 4.223733 | 3.705119 | -1.301341 |
| C | 2.248429 | -1.091817 | -2.252473 |
| C | 1.516529 | -1.406731 | -0.922865 |
| H | 7.599111 | 1.952212 | -1.503755 |
| H | 2.413855 | 2.314095 | -0.119451 |
| H | 3.561863 | 1.627823 | 1.049809 |
| H | 7.330353 | 4.195998 | -2.56597 |
| H | 1.013898 | 0.592376 | -0.204295 |
| H | 1.85393 | -0.387187 | 1.030546 |
| H | 5.098374 | 5.344066 | -2.397061 |
| H | 2.361554 | 1.098422 | -2.364916 |
| H | 3.959494 | 0.310608 | -2.458258 |
| H | 3.245019 | 4.165691 | -1.213924 |
| H | 1.558621 | -1.010462 | -3.094782 |
| H | 2.967636 | -1.876068 | -2.491919 |
| H | 1.923926 | -2.306985 | -0.461364 |
| H | 0.445004 | -1.562361 | -1.0626 |

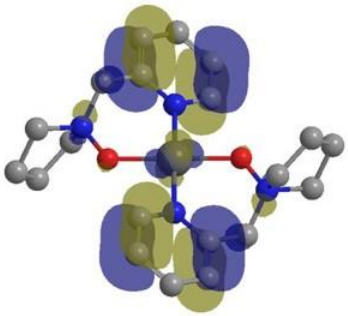
**Valence orbitals and LUMO of 1 with energies in Hartrees**



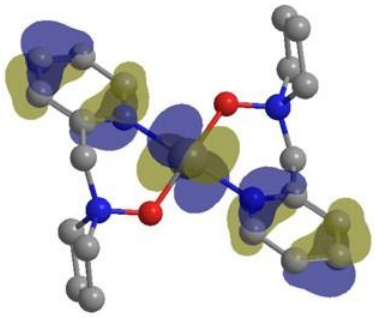
HOMO – 1 (-0.47441)



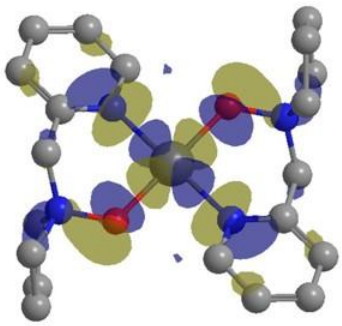
HOMO (-0.45577)



HOMO – 3 (-0.49935)



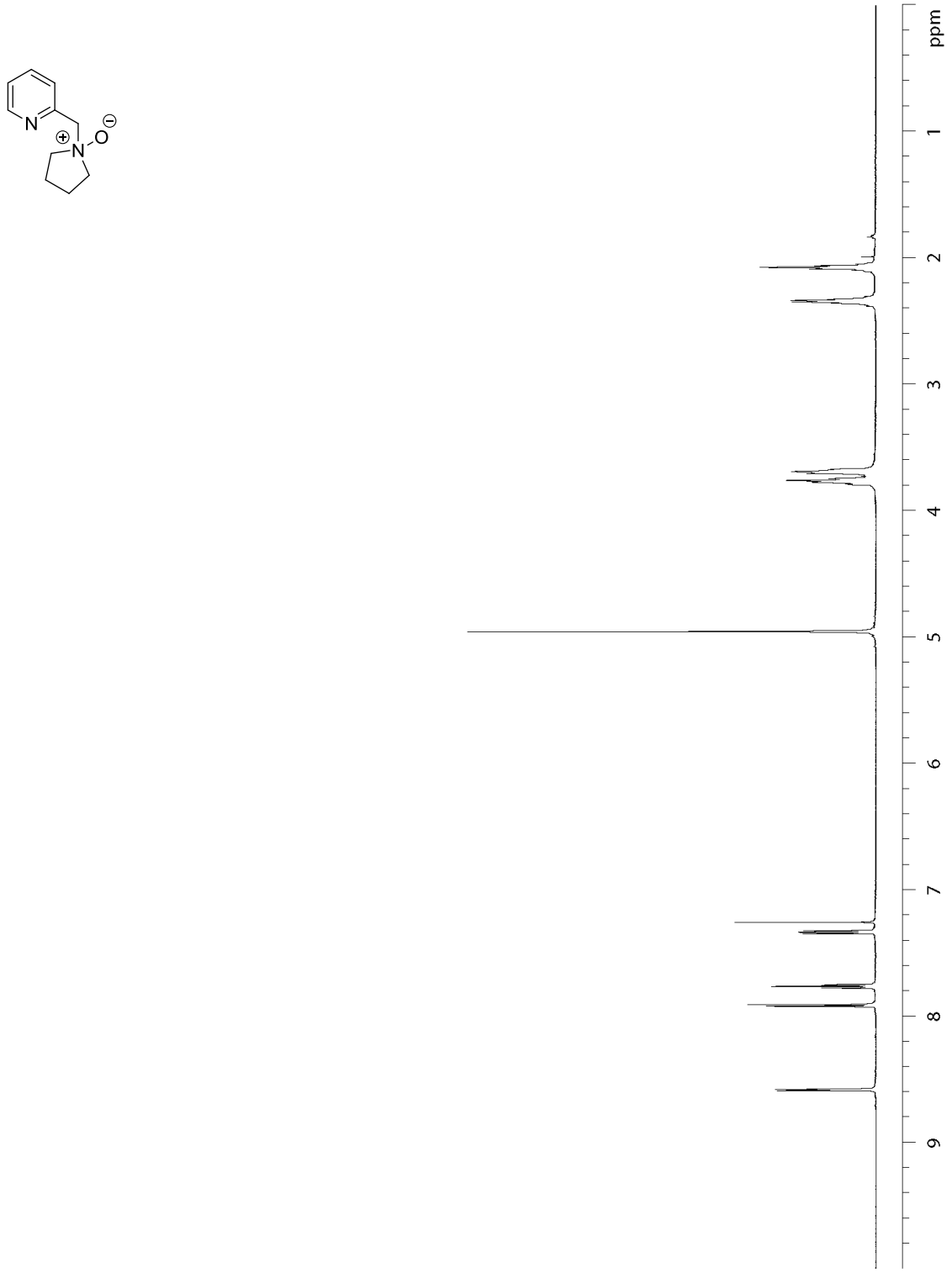
HOMO – 2 (-0.49032)



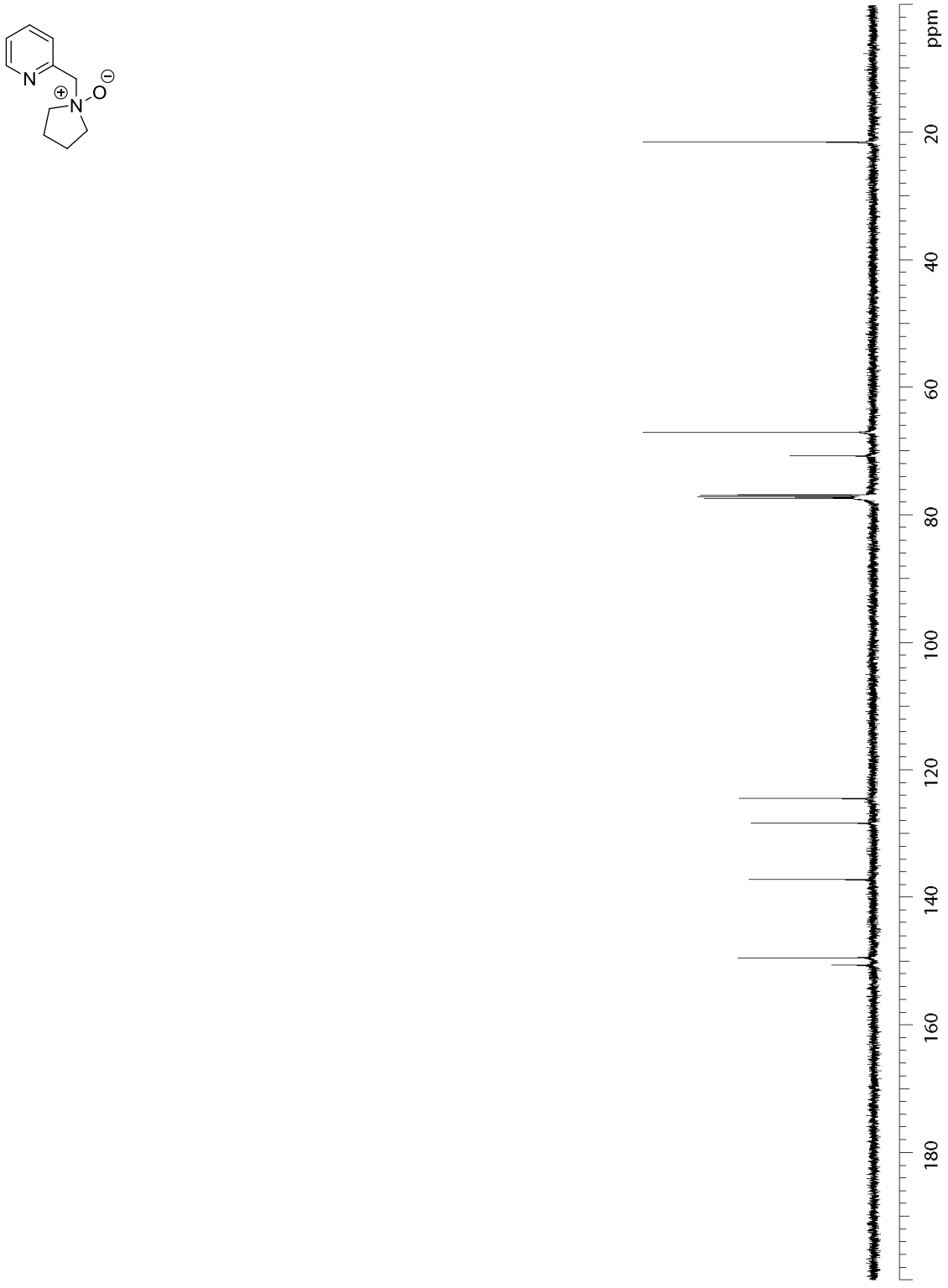
LUMO (-0.29227)

## Spectroscopic Data

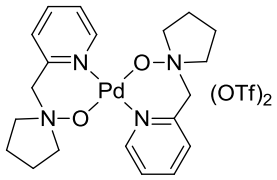
$^1$H NMR ($CDCl_3$, 23 ºC) of **S2**

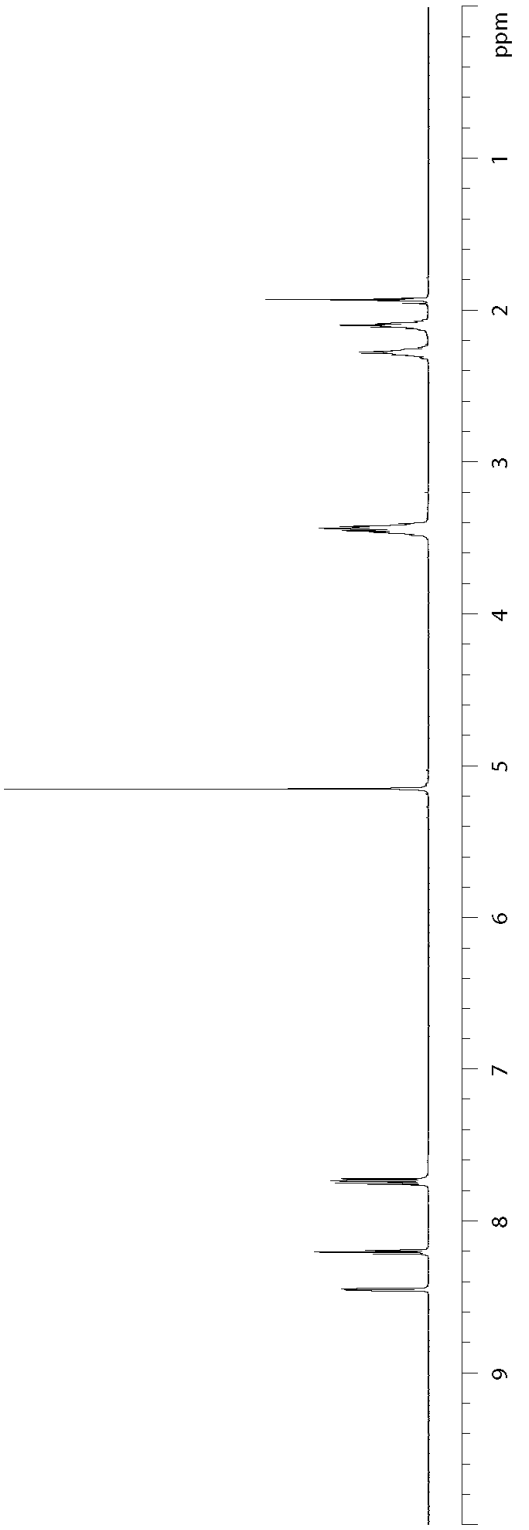


$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **S2**

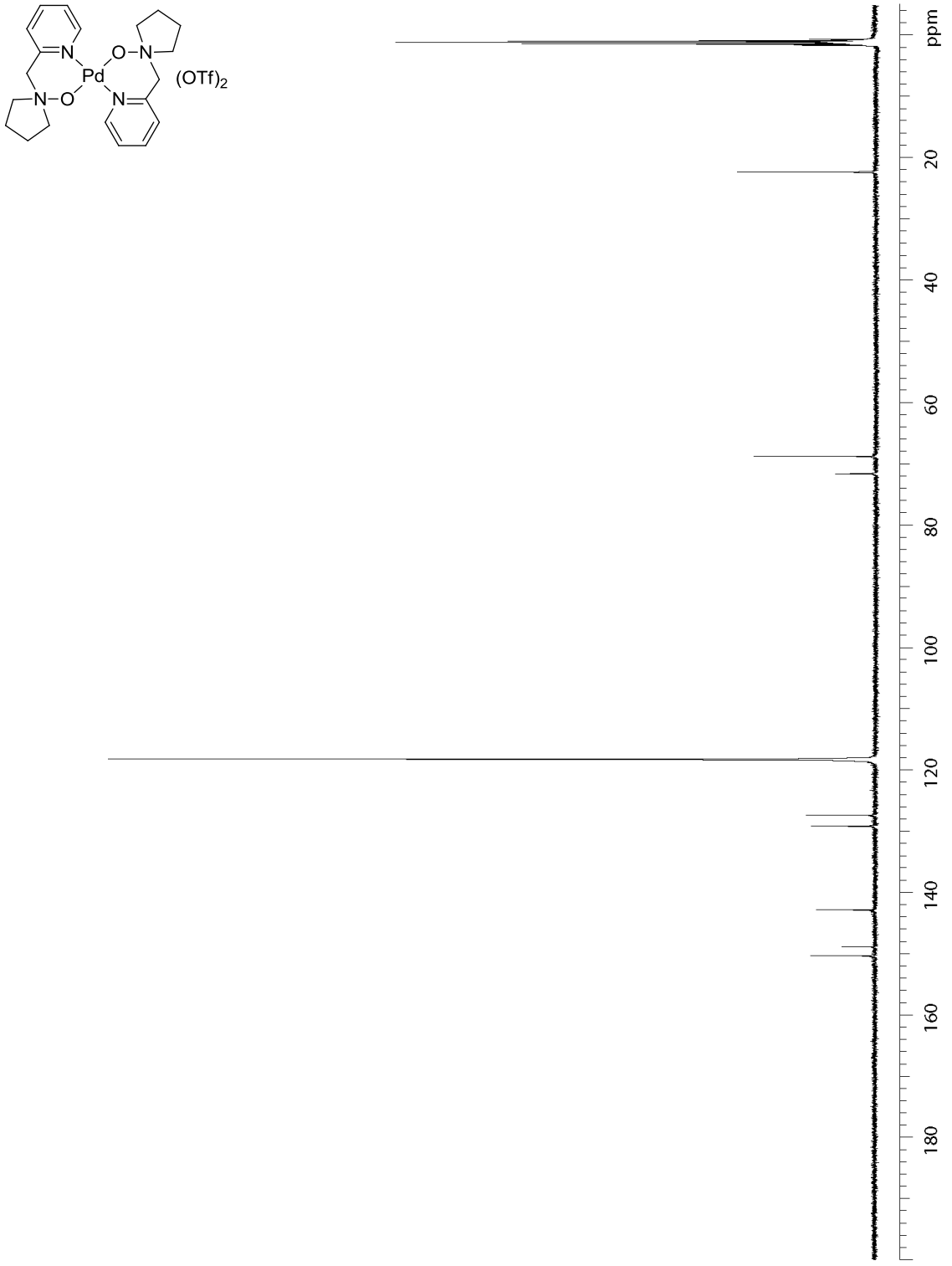


$^1$H NMR ($CD_3CN$, 23 ºC) of palladium complex **1**

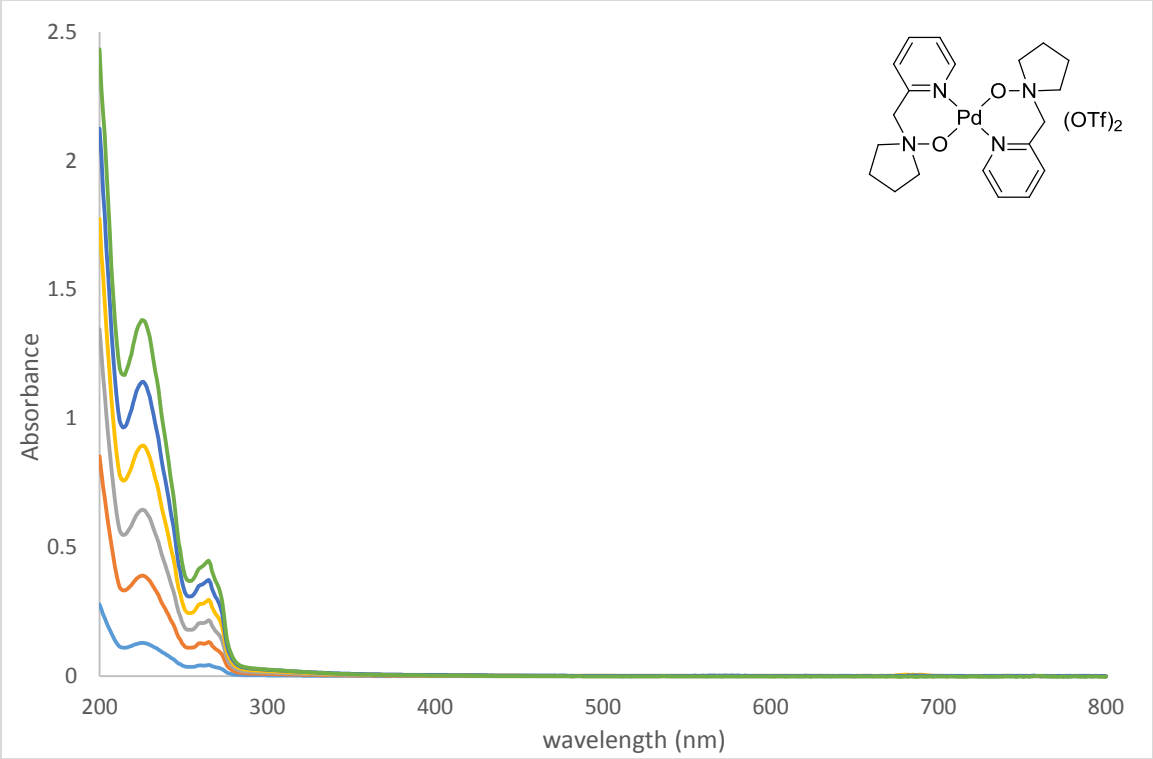


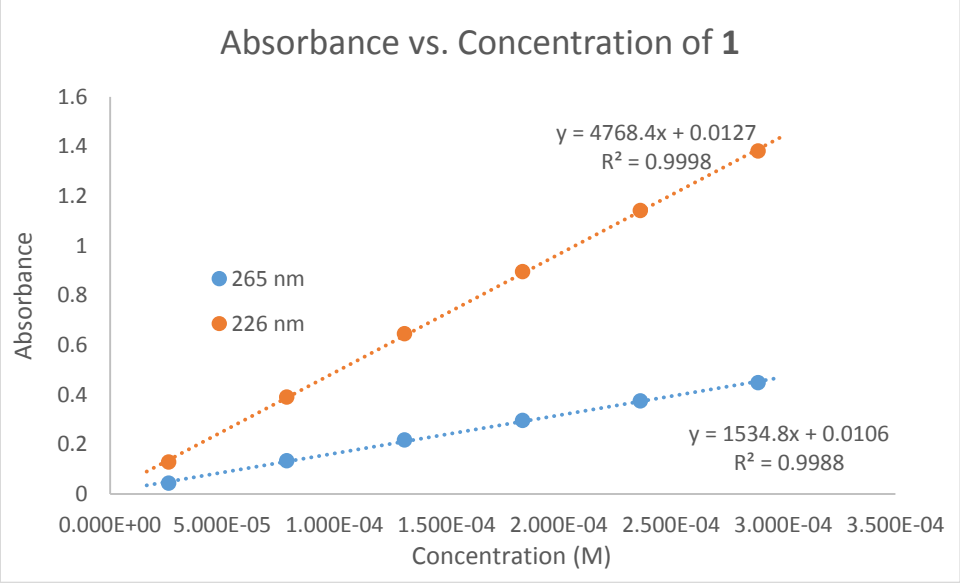



$^{13}C$ NMR ($CD_3CN$, 23 ºC) of palladium complex **1**

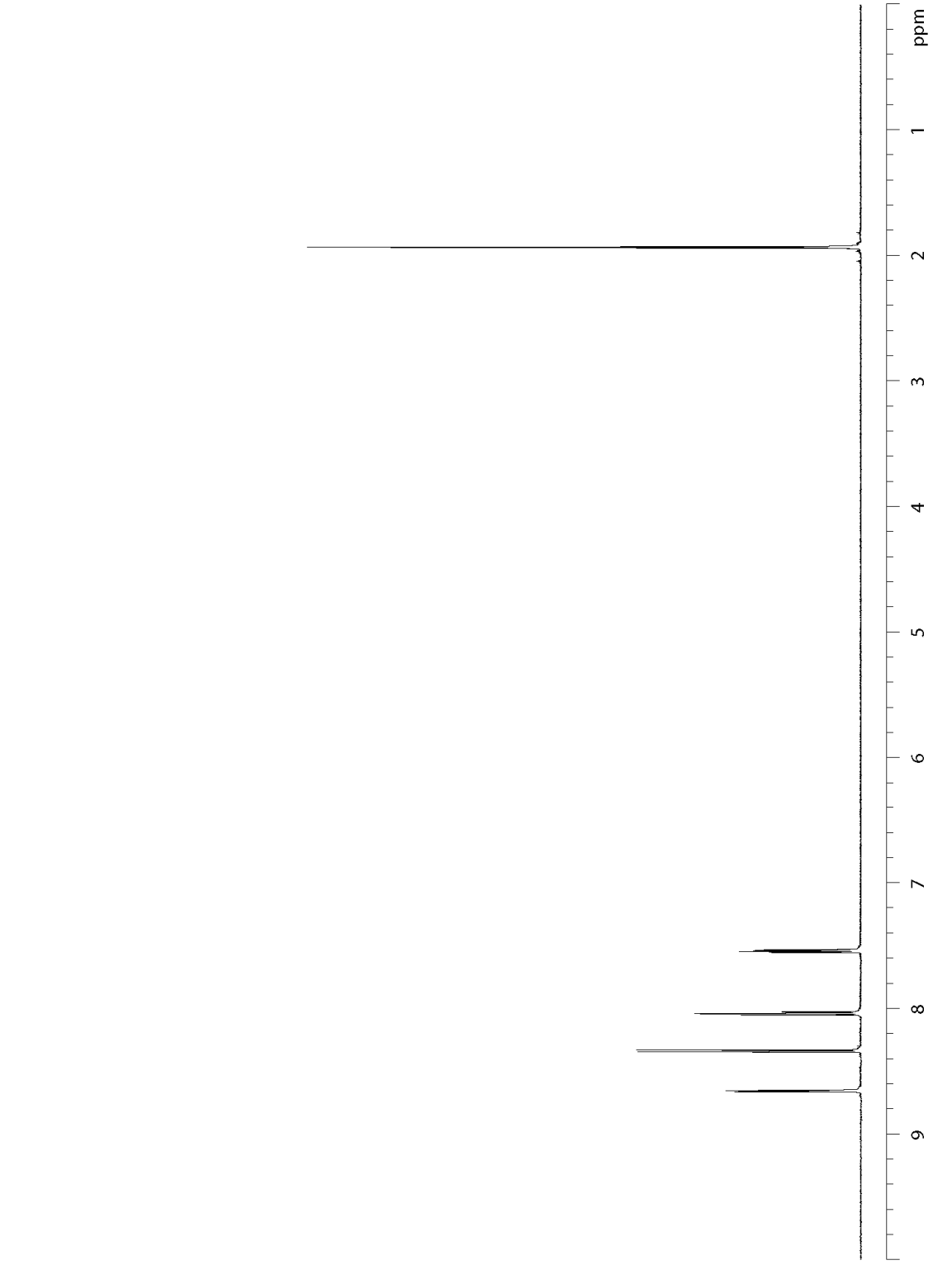


UV/vis of palladium complex **1**

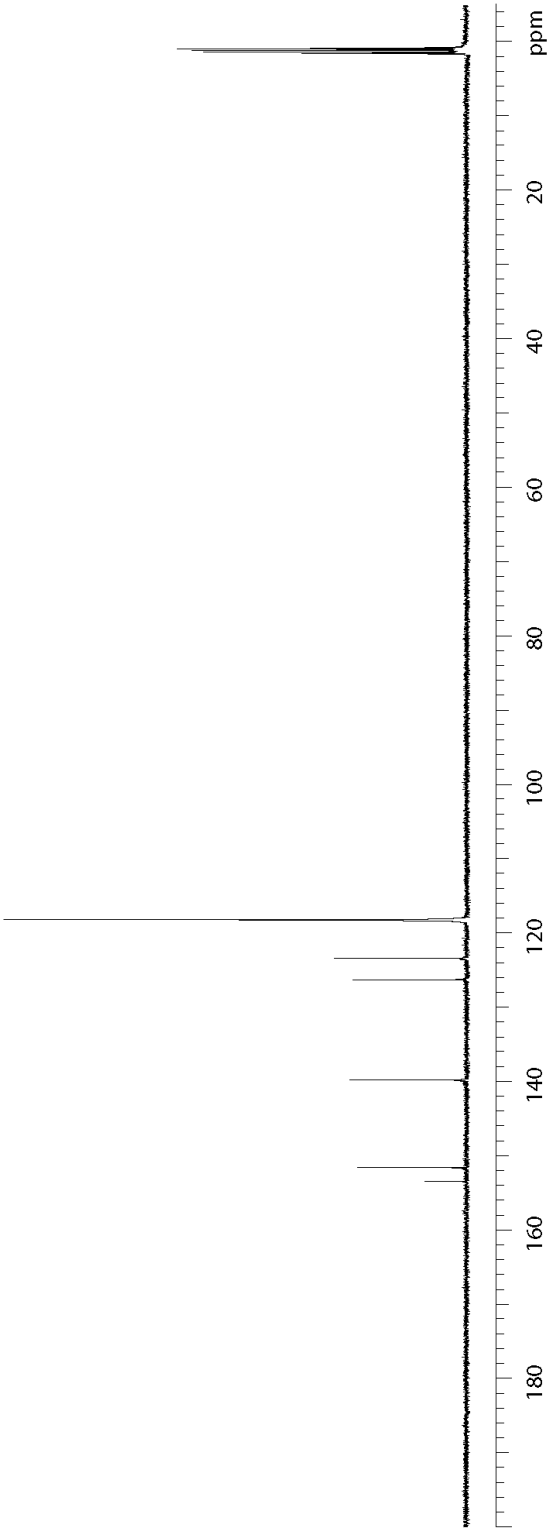


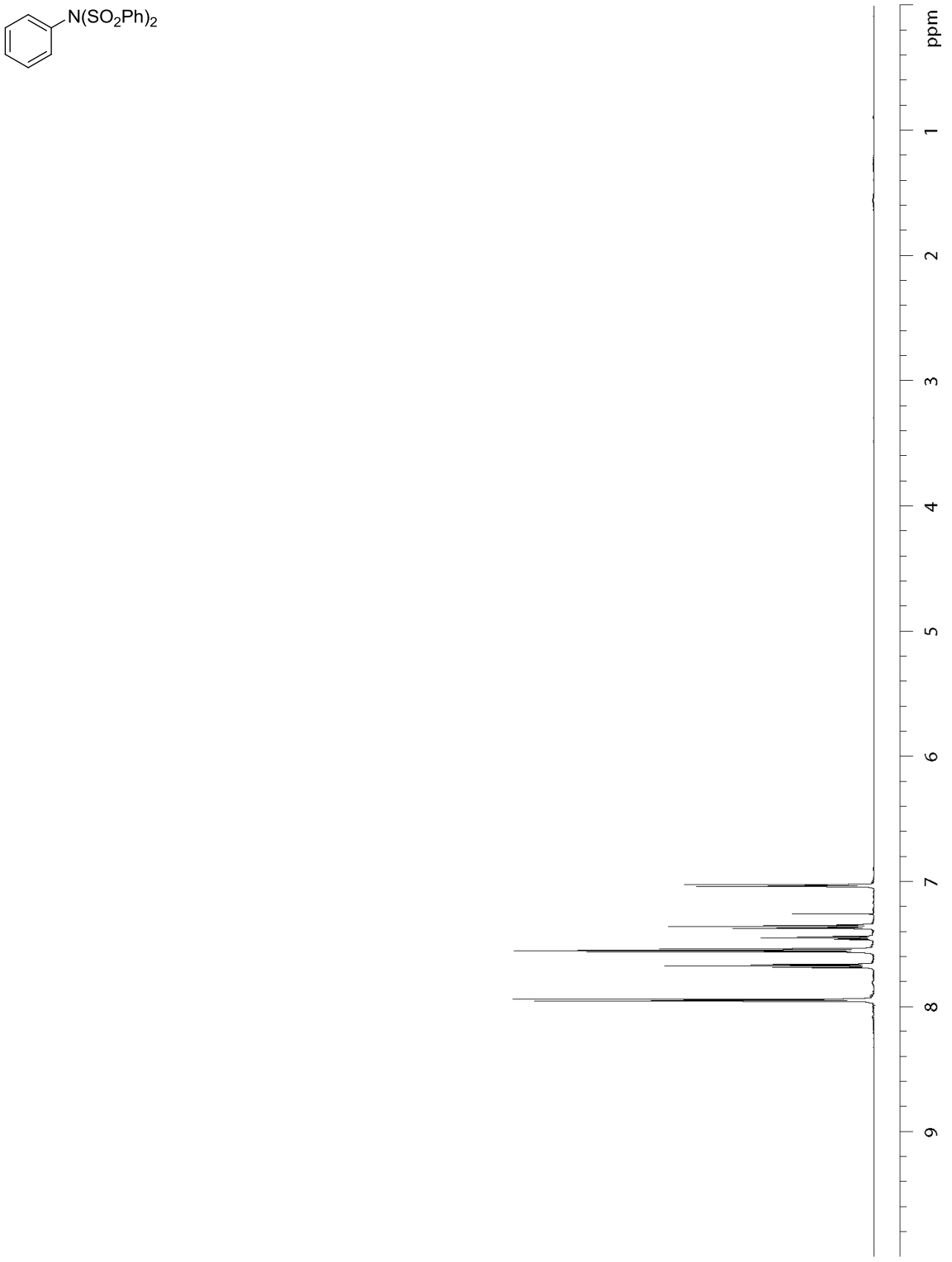
$^{1}$H NMR ($CD_3CN$, 23 ºC) of $Ag(bipy)_2ClO_4$



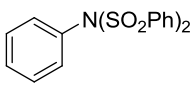
$^{13}C$ NMR ($CD_3CN$, 23 ºC) of $Ag(bipy)_2ClO_4$

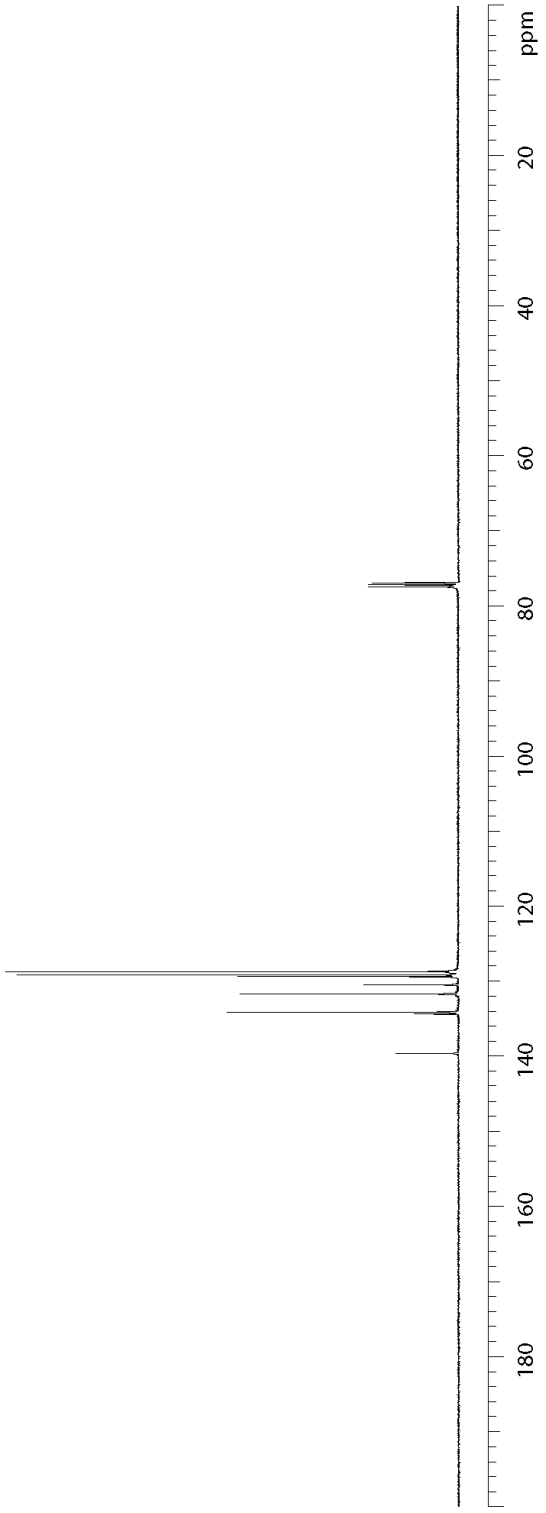


$^1$H NMR ($CDCl_3$, 23 ºC) of **2a**

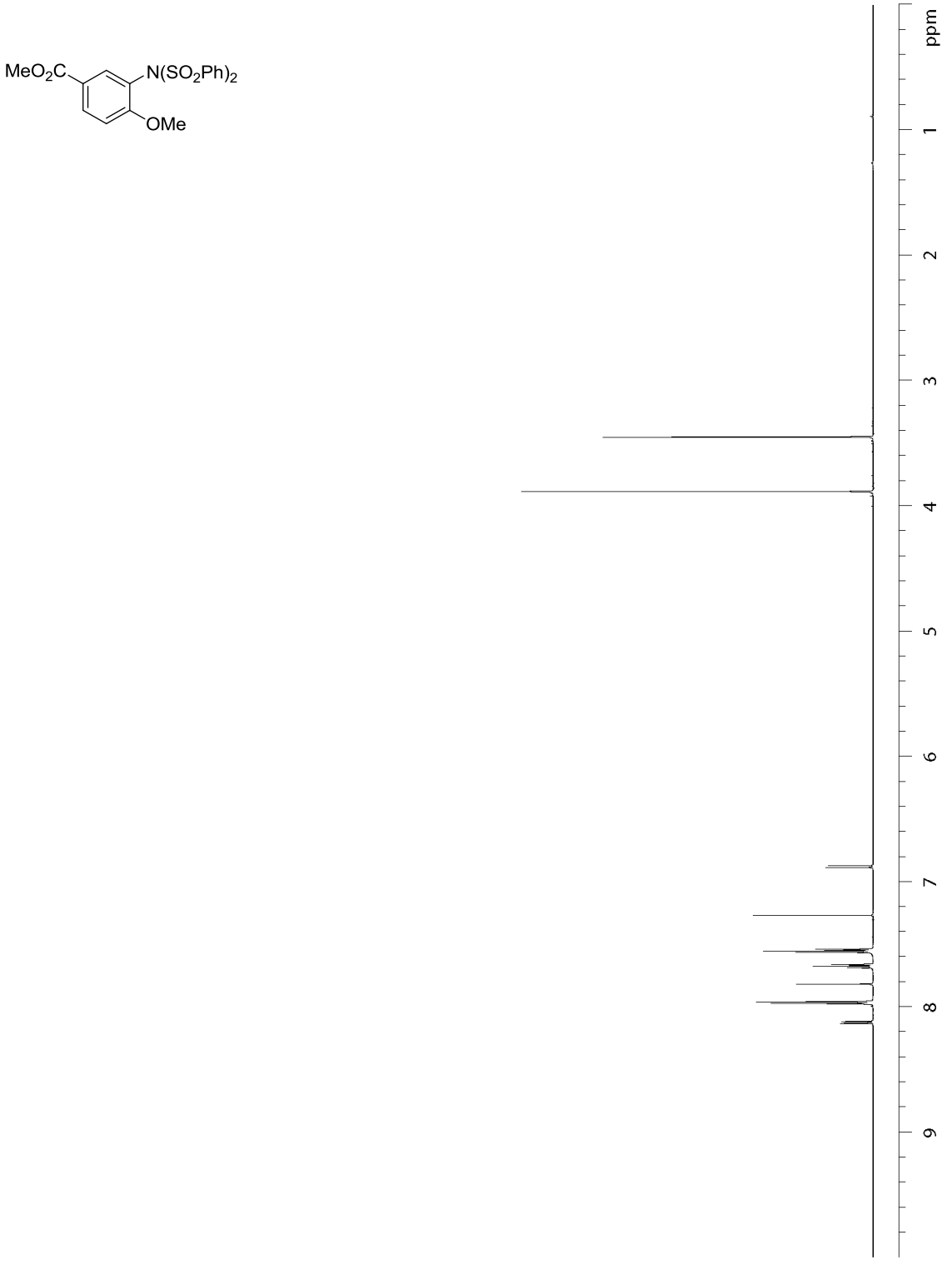


$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2a**

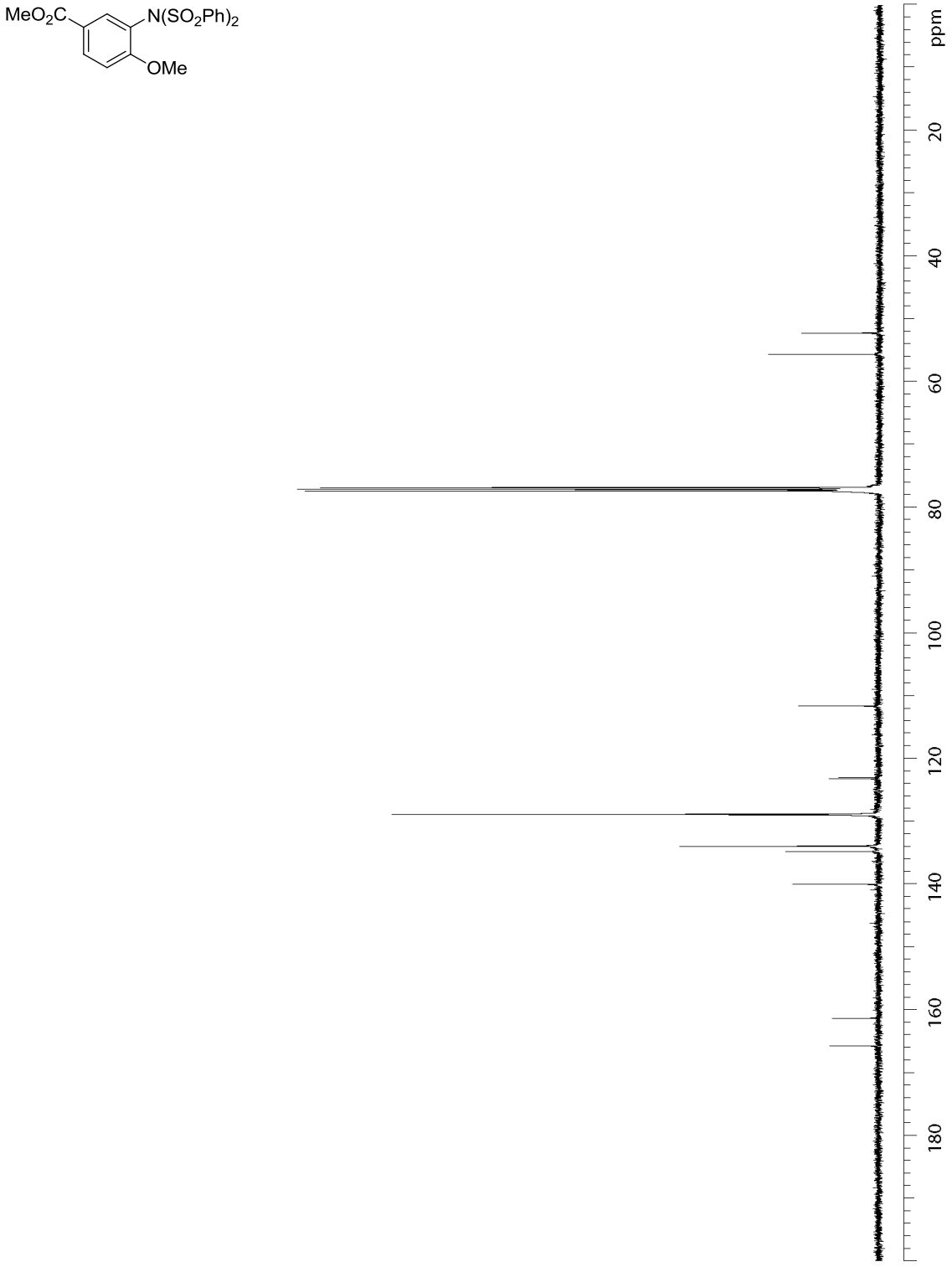


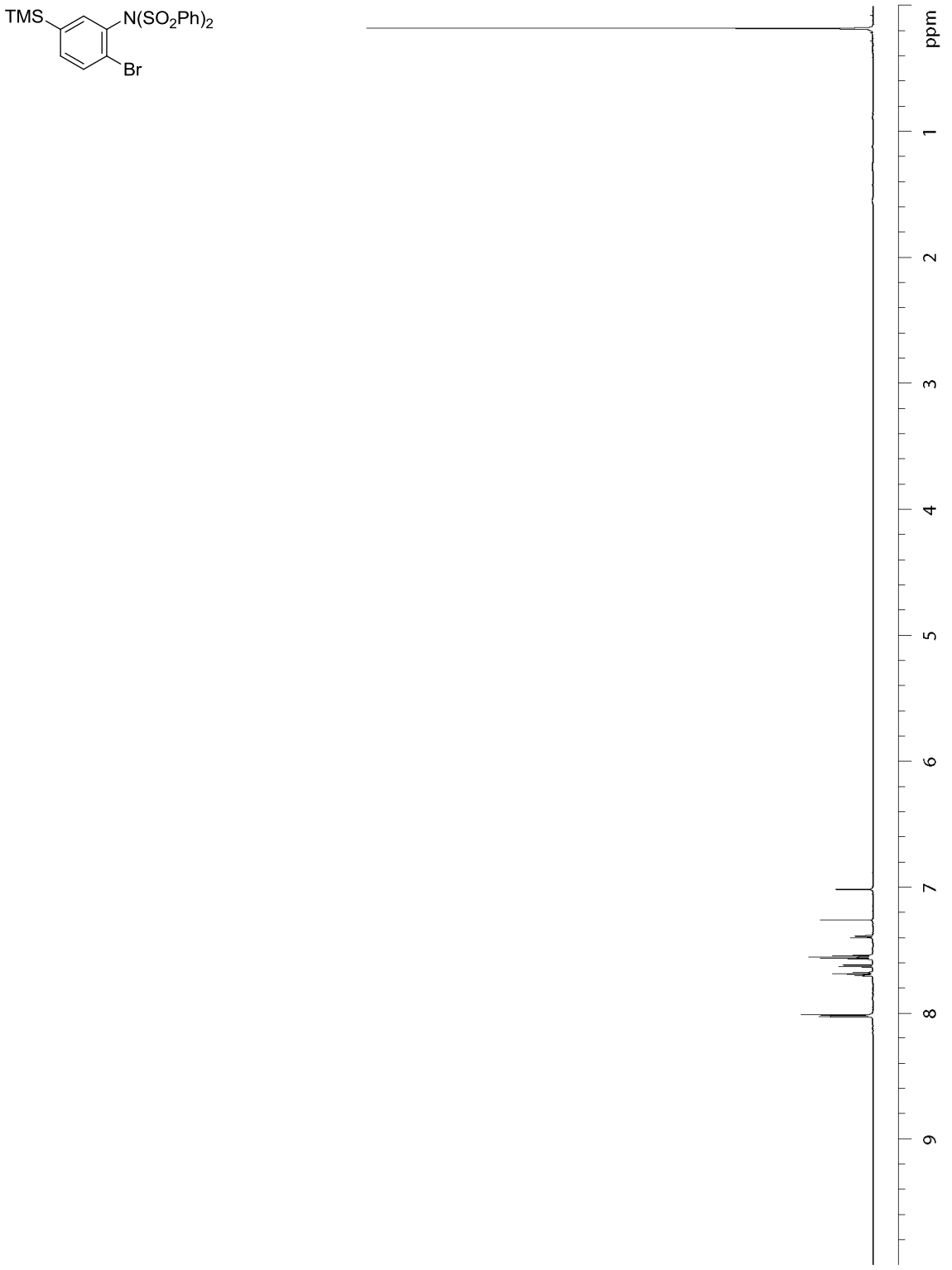
$^1$H NMR ($CDCl_3$, 23 ºC) of **2b**



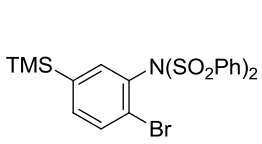
$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2b**

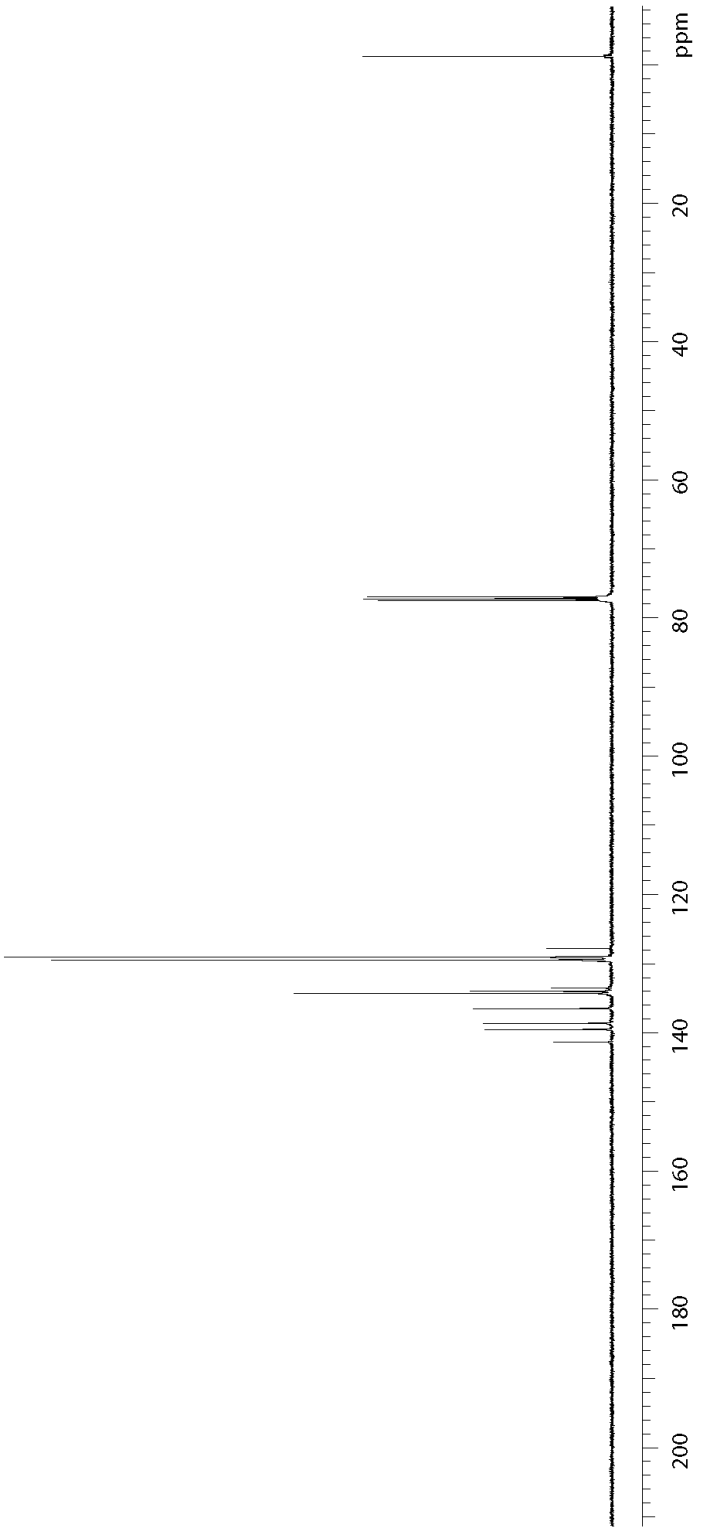


$^1$H NMR ($CDCl_3$, 23 ºC) of **2c**

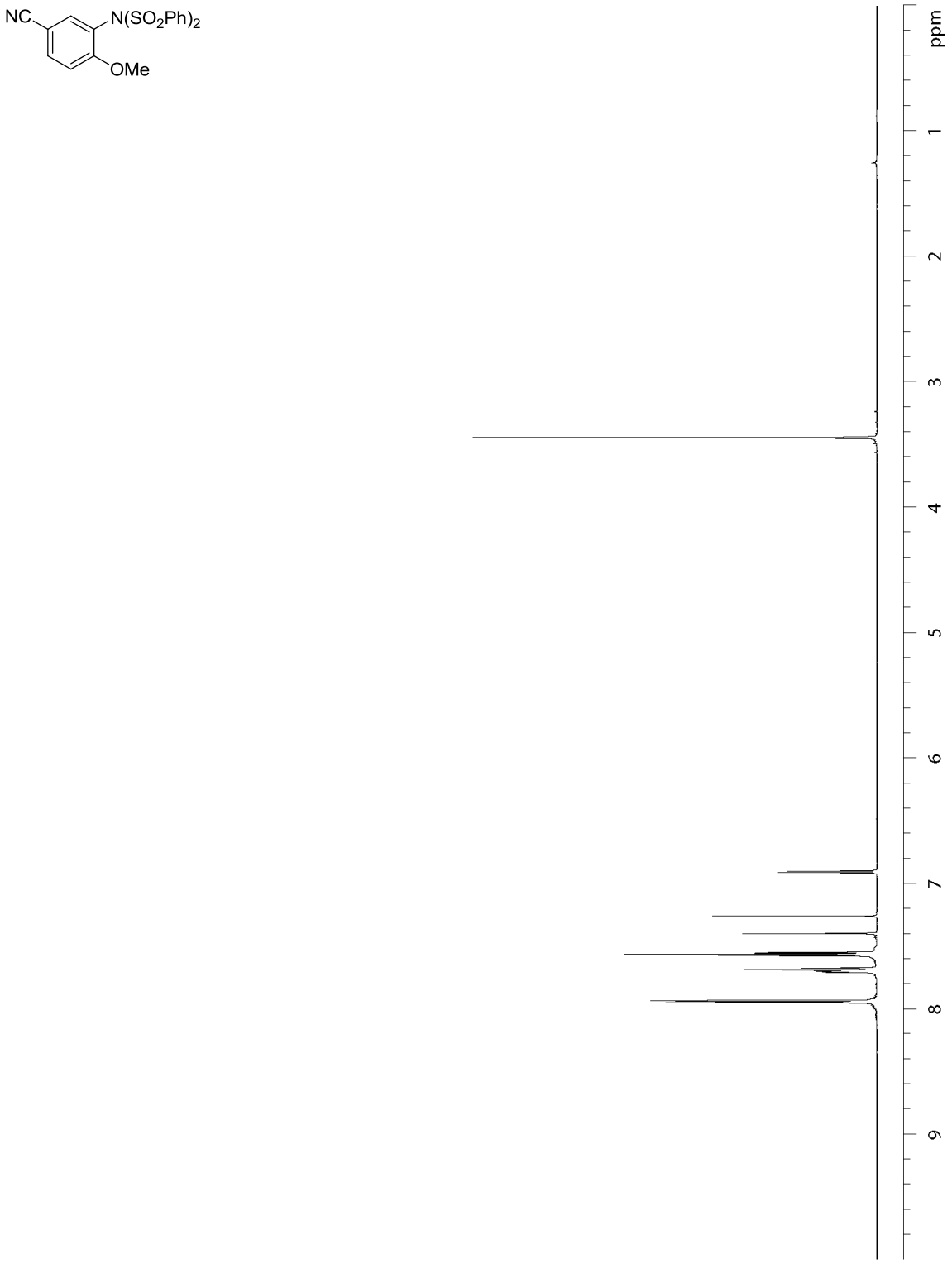


$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2c**

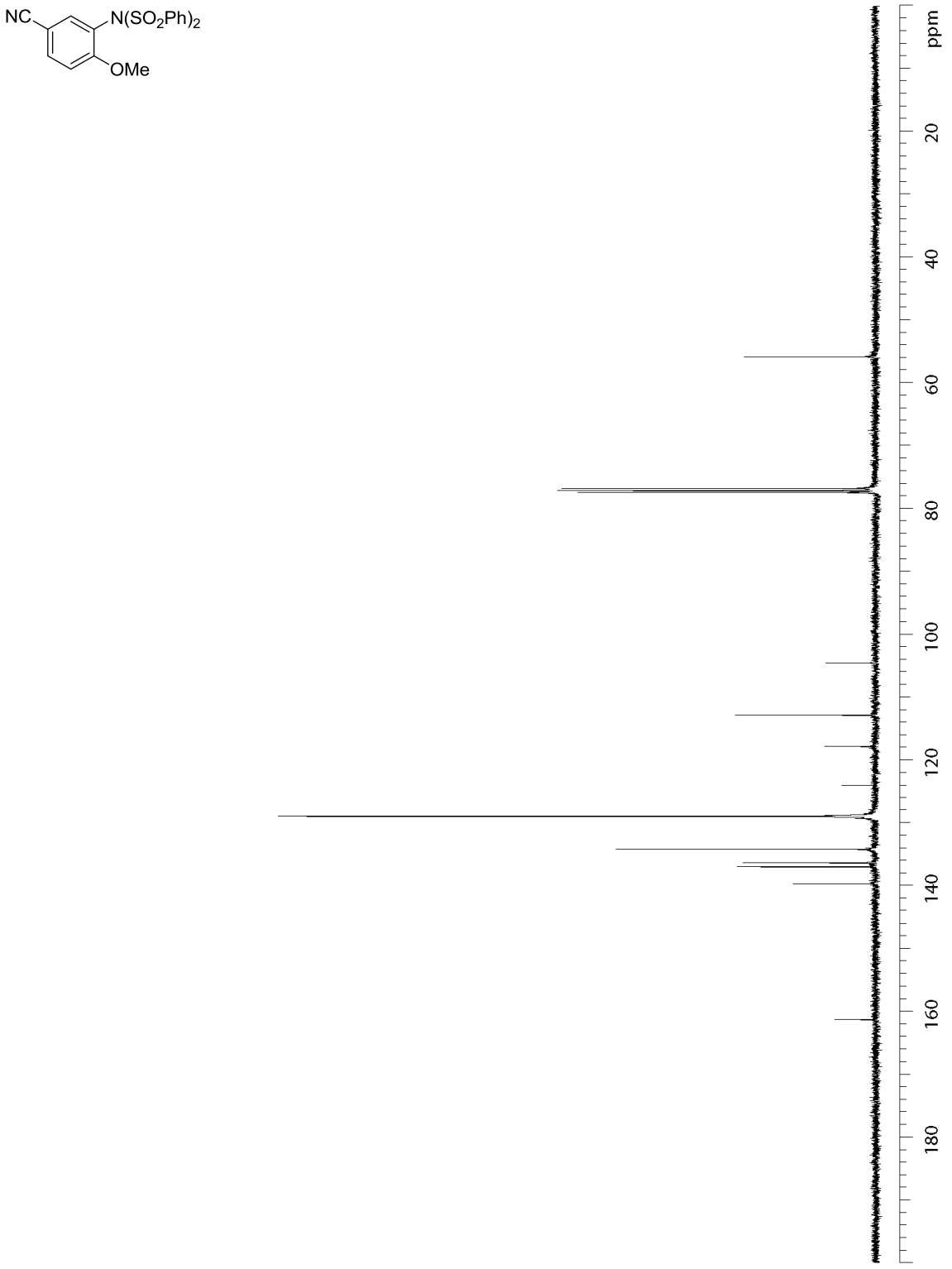


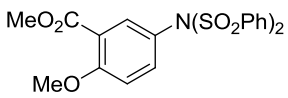
$^1$H NMR ($CDCl_3$, 23 ºC) of **2d**

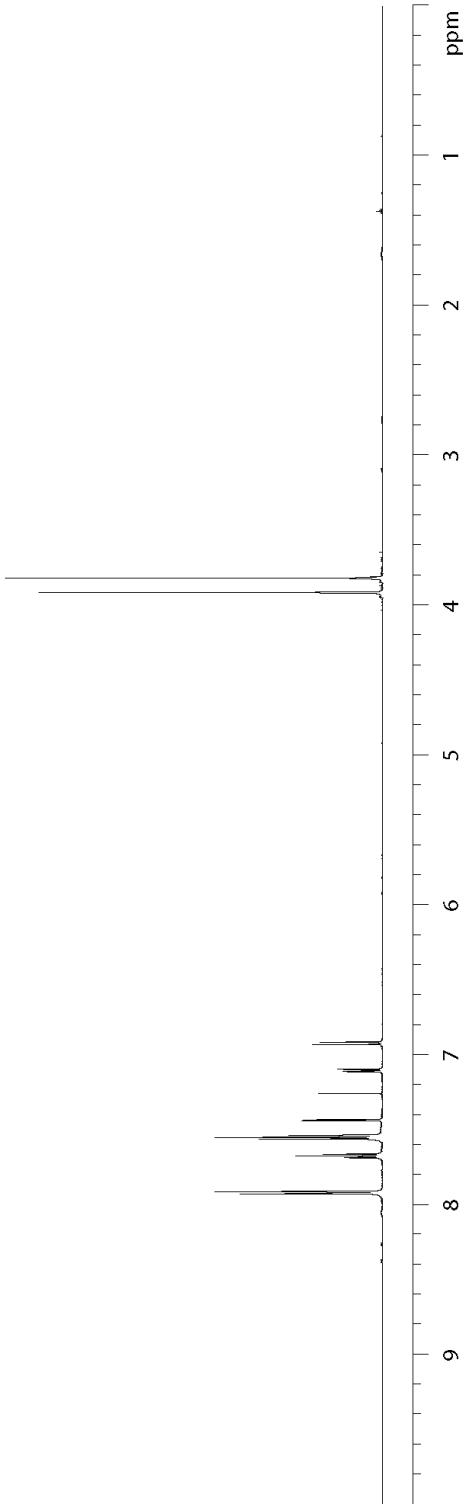


$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2d**

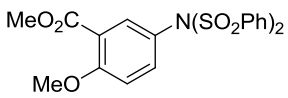


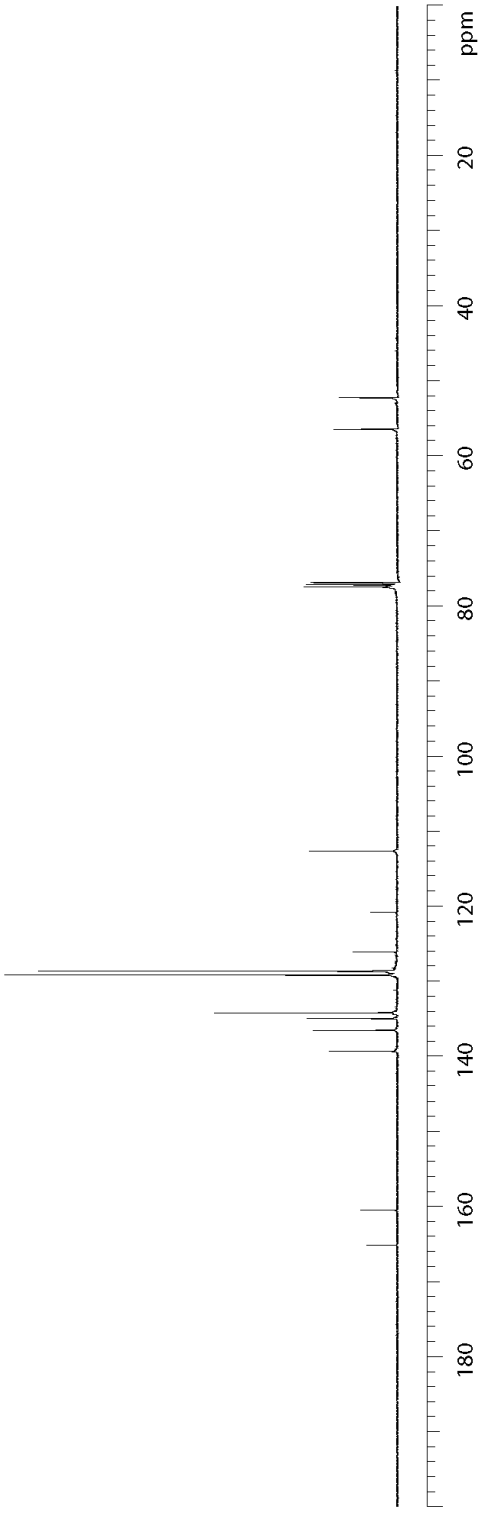
$^1$H NMR ($CDCl_3$, 23 ºC) of **2e**



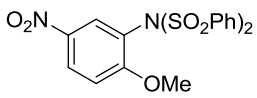



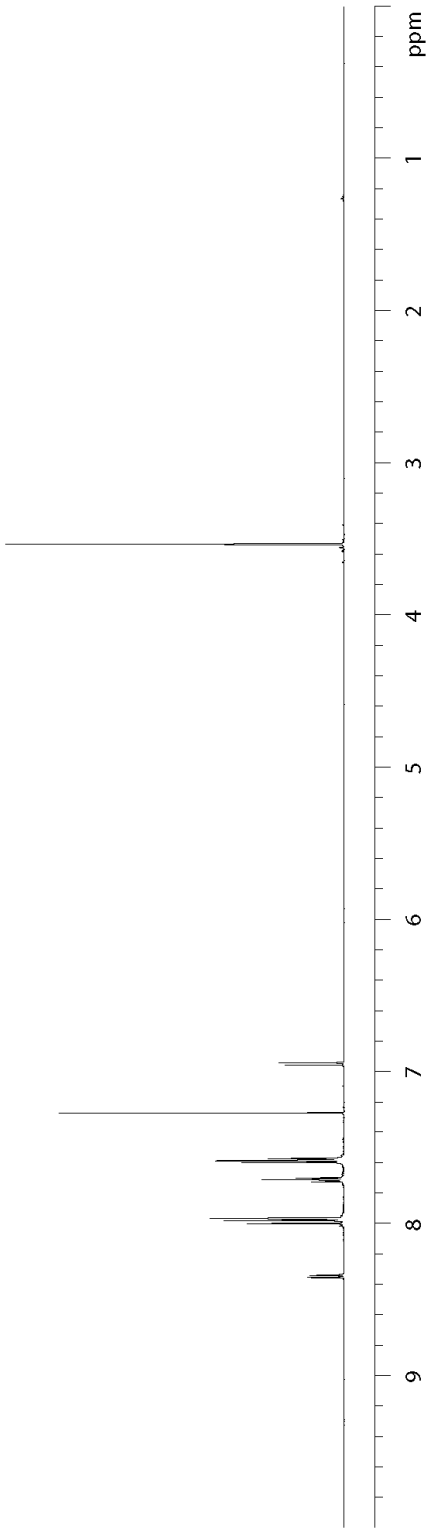
$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2e**



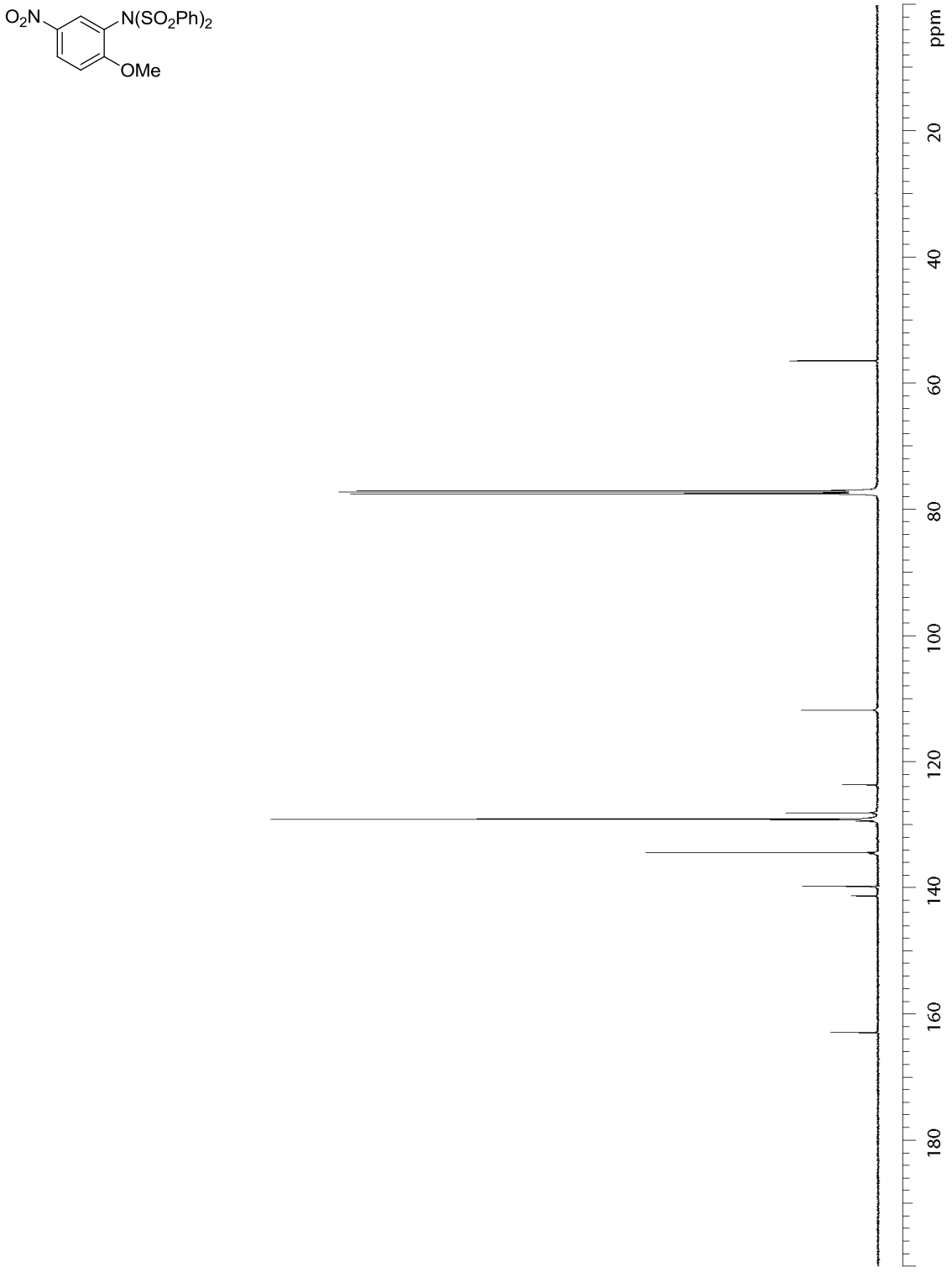



$^1$H NMR ($CDCl_3$, 23 ºC) of **2f**

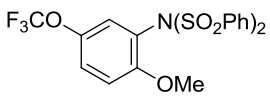


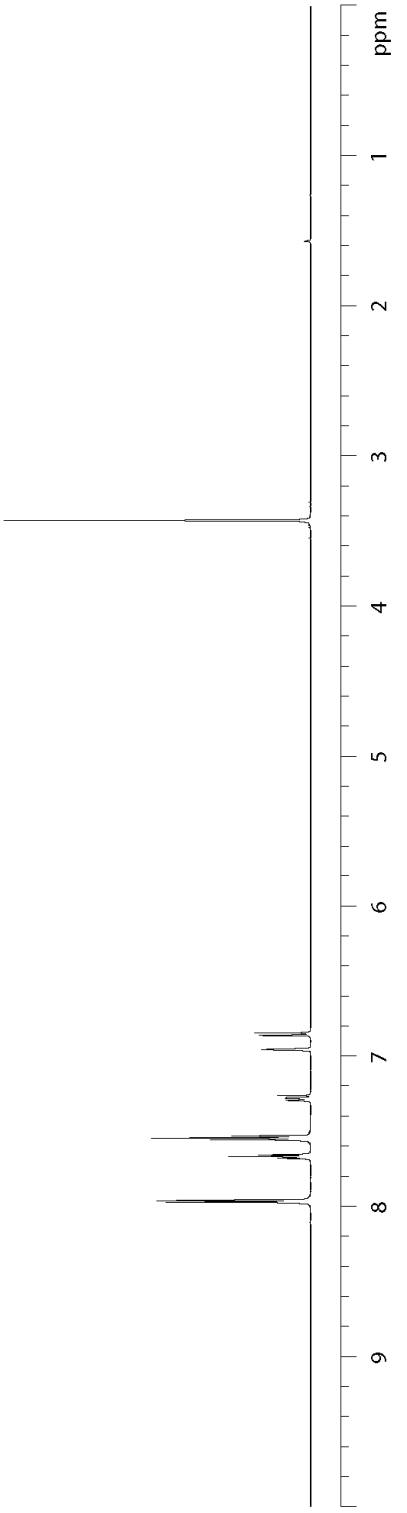



$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2f**

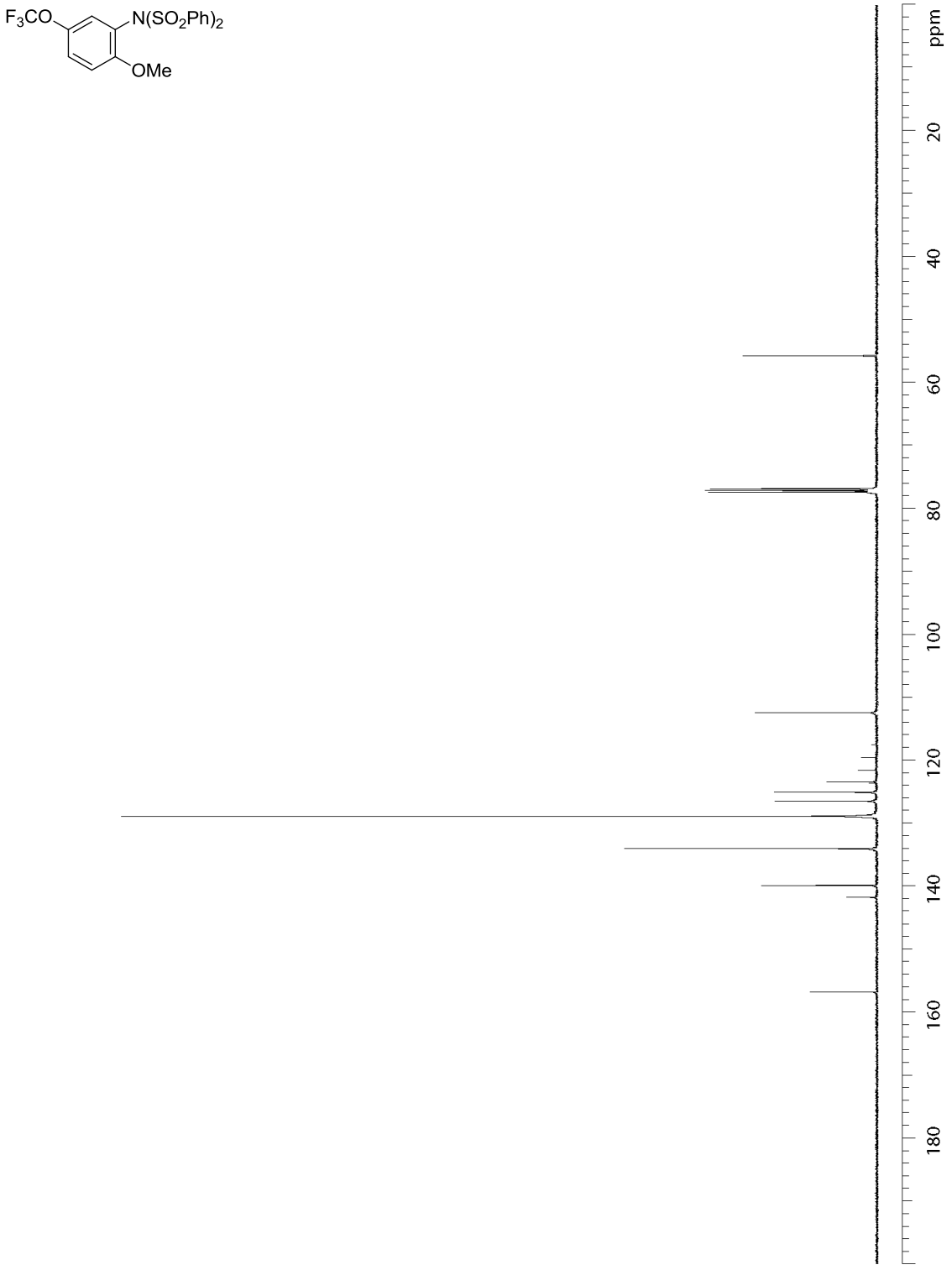


$^1$H NMR ($CDCl_3$, 23 ºC) of **2g**

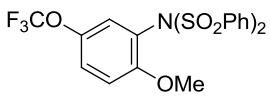


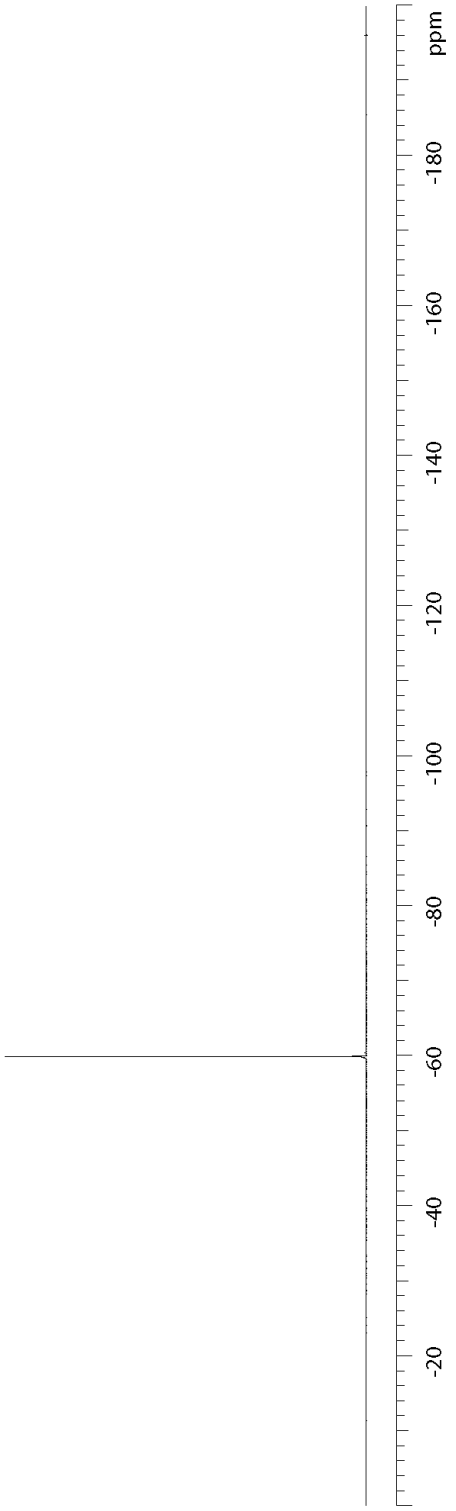



$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2g**

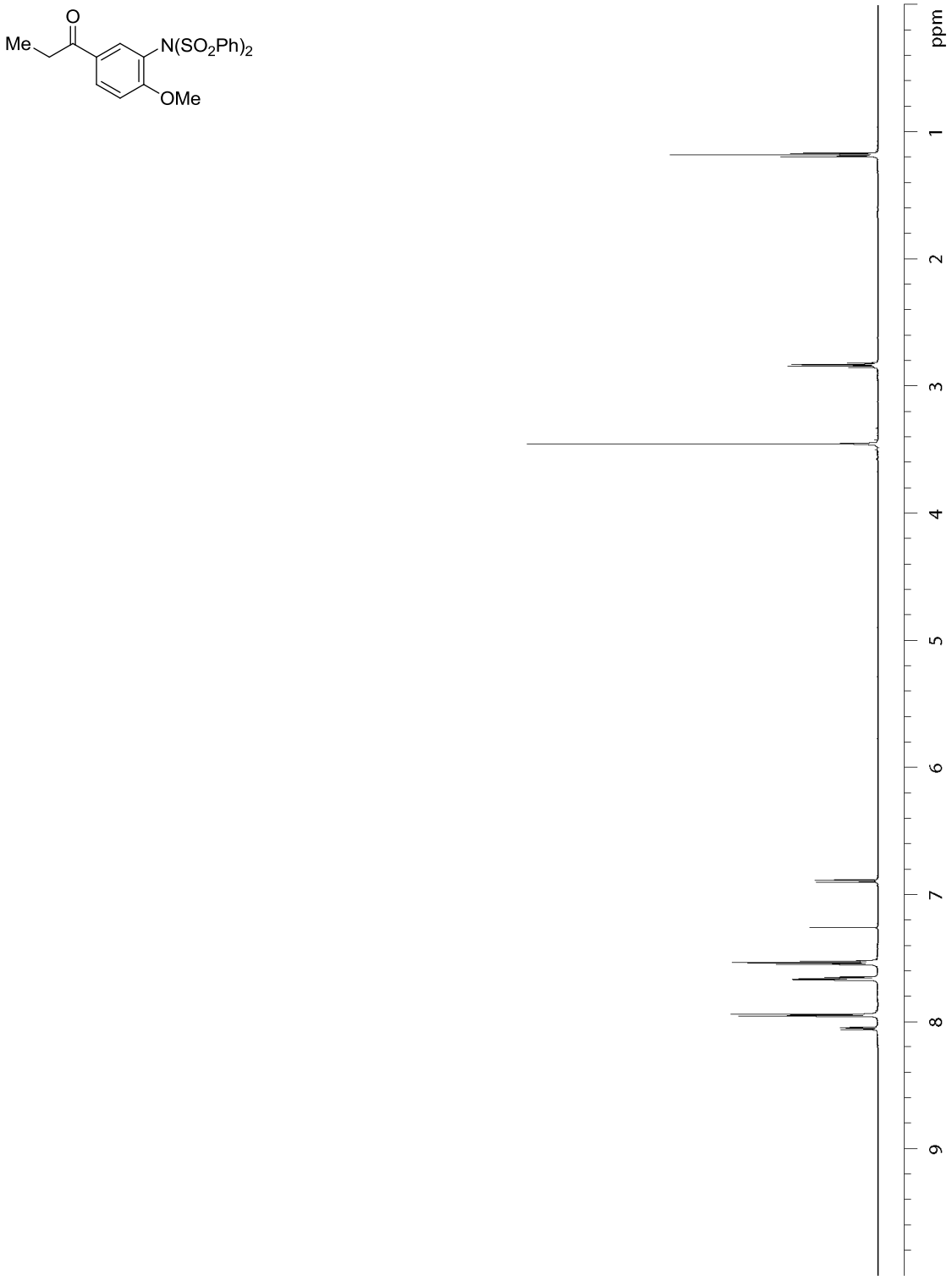


$^{19}F$ NMR ($CDCl_3$, 23 ºC) of **2g**

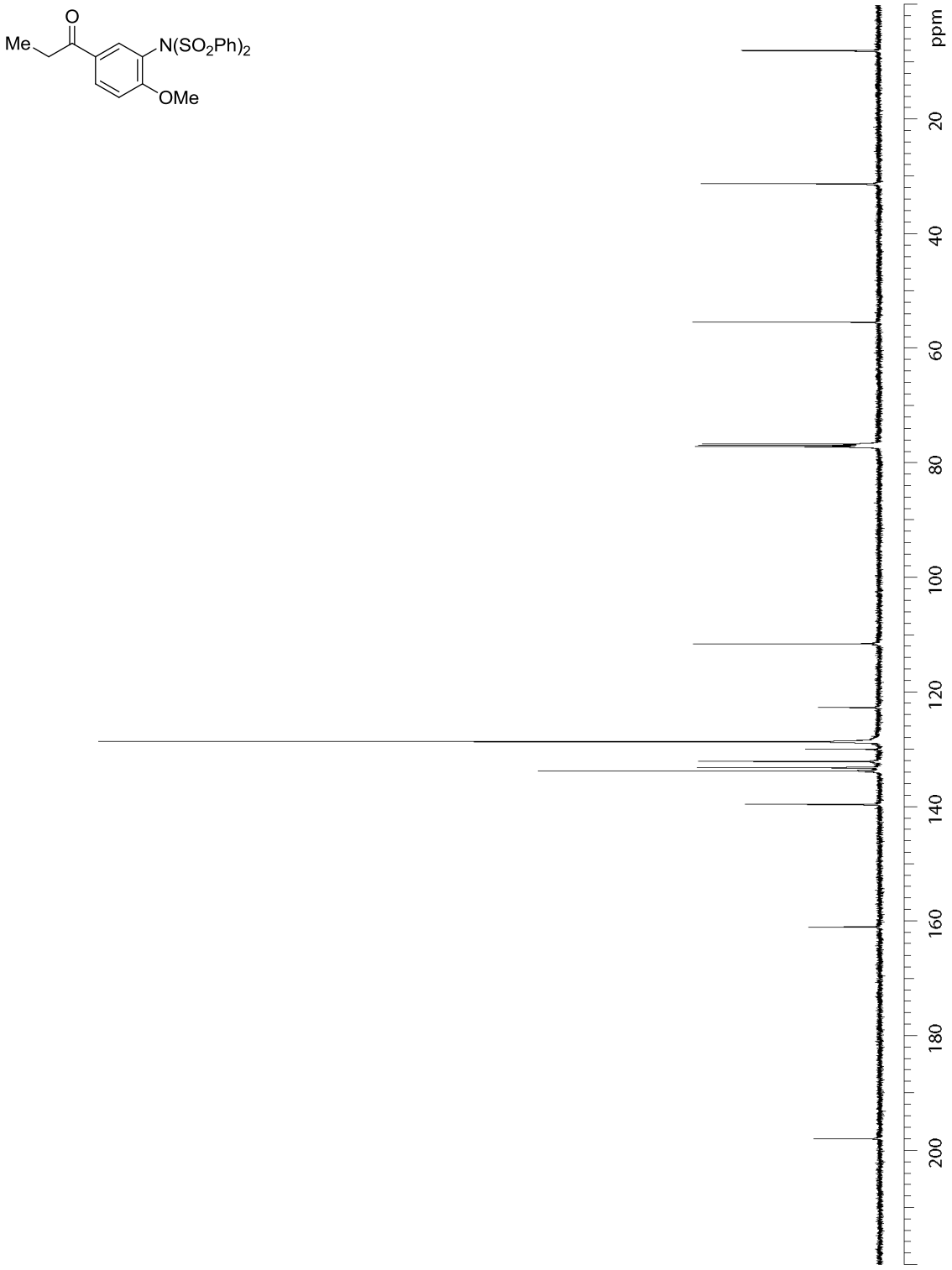


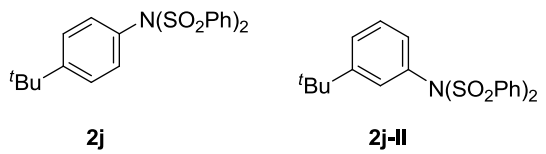
$^1$H NMR ($CDCl_3$, 23 ºC) of **2h**



$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2h**



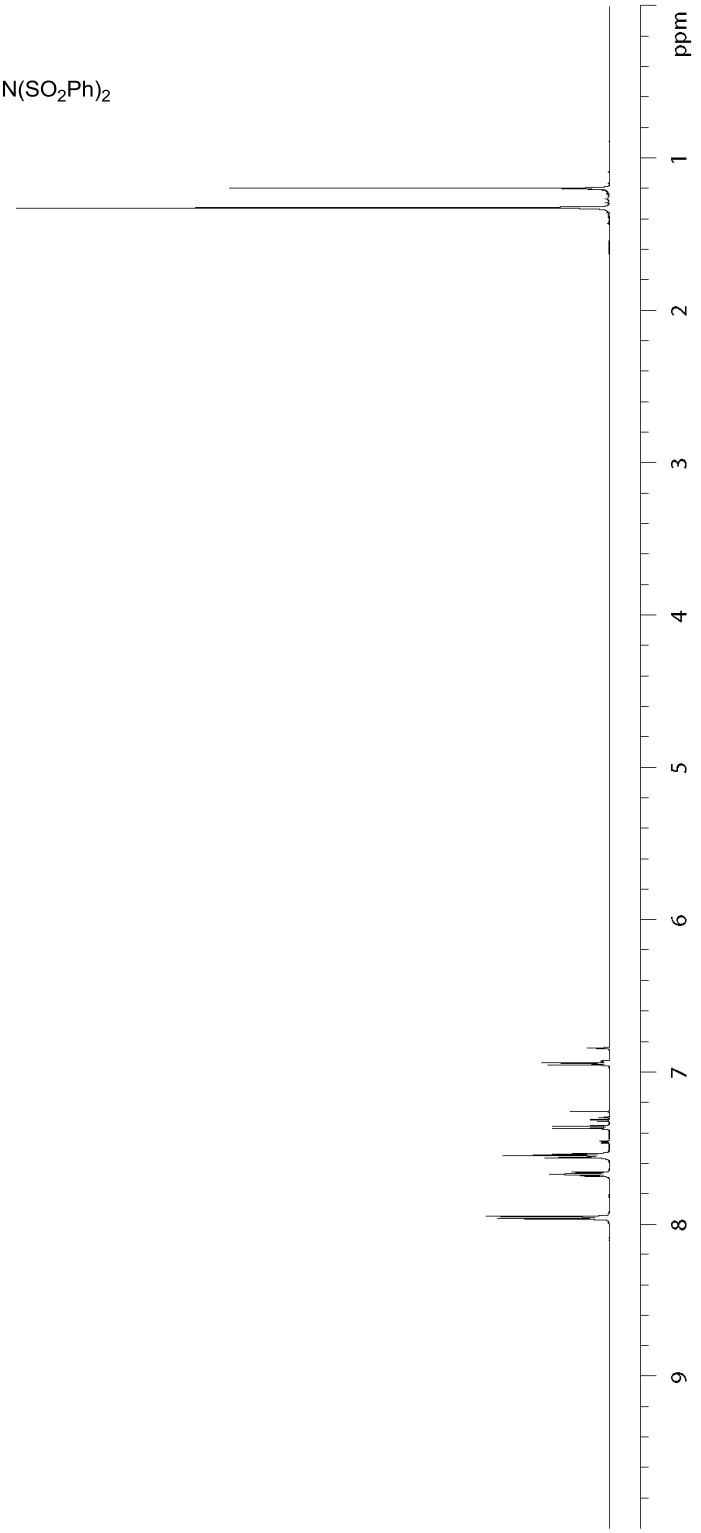
$^1$H NMR ($CDCl_3$, 23 ºC) of **2j** and **2j-II**



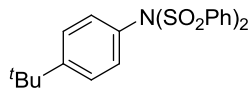

**2j**



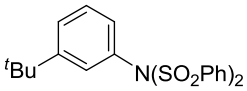

**2j-II**



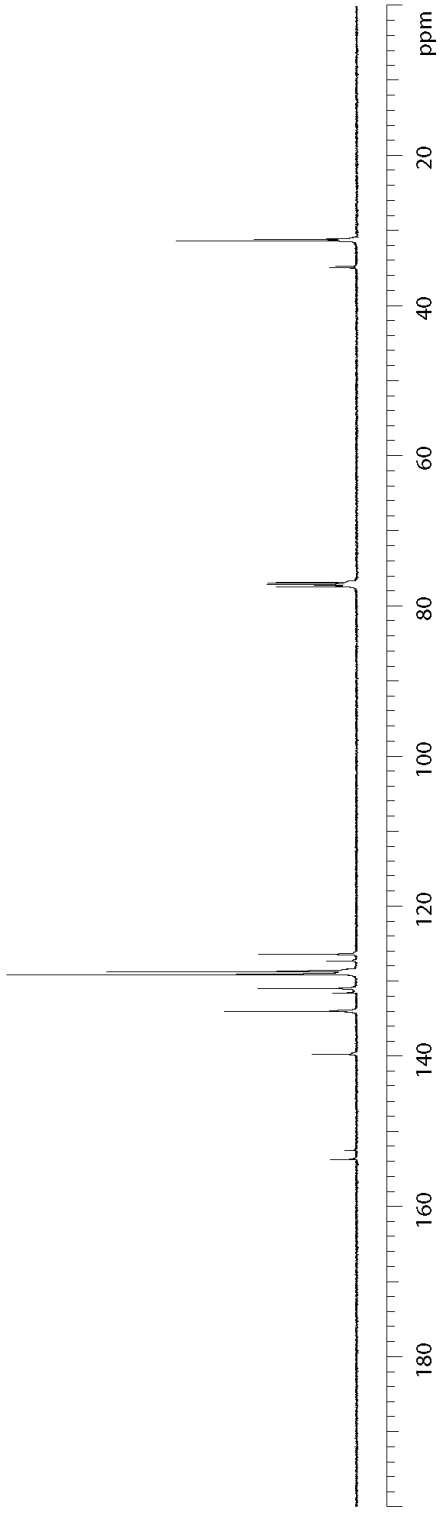
$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2j** and **2j-II**



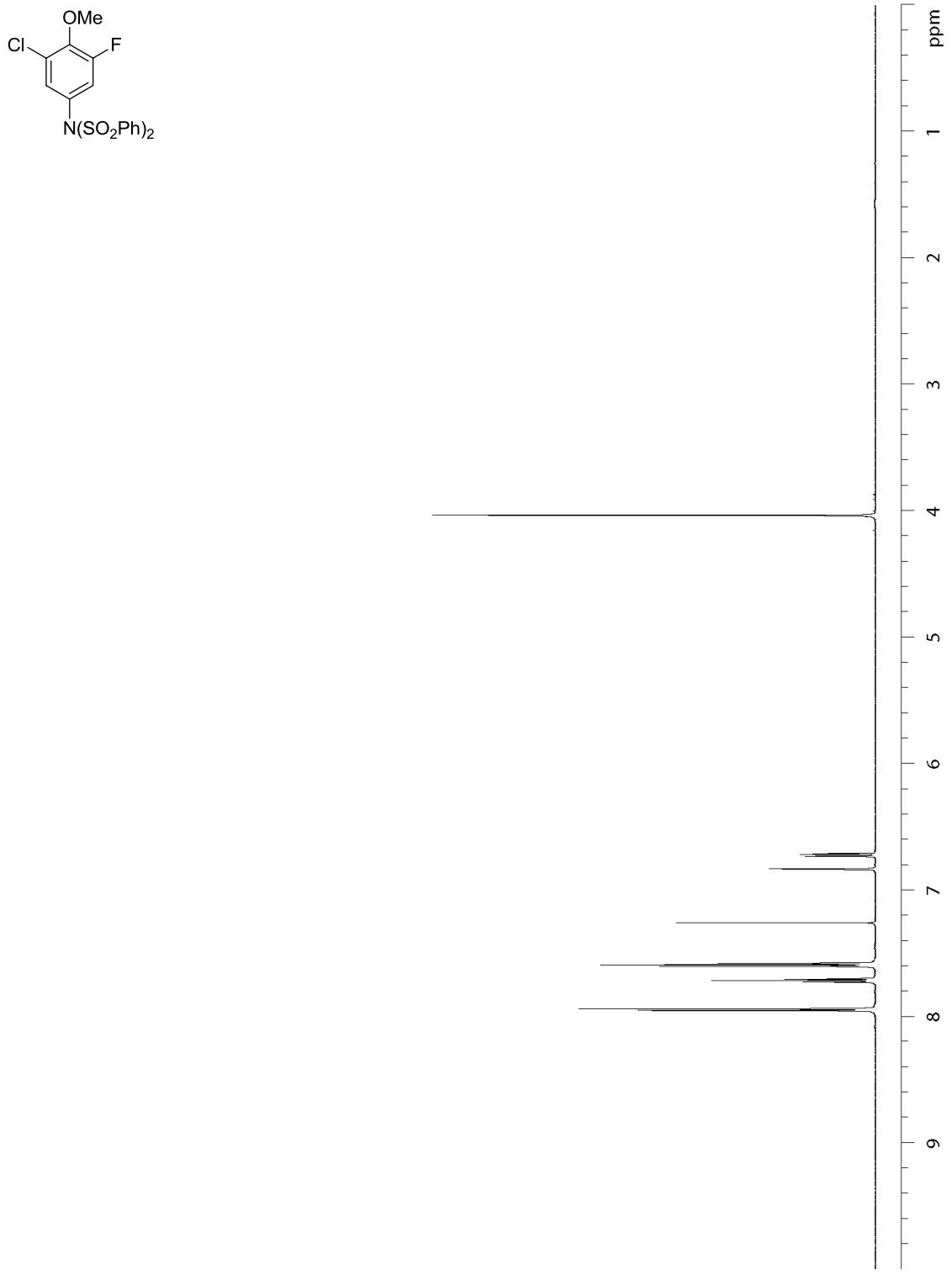

**2j**



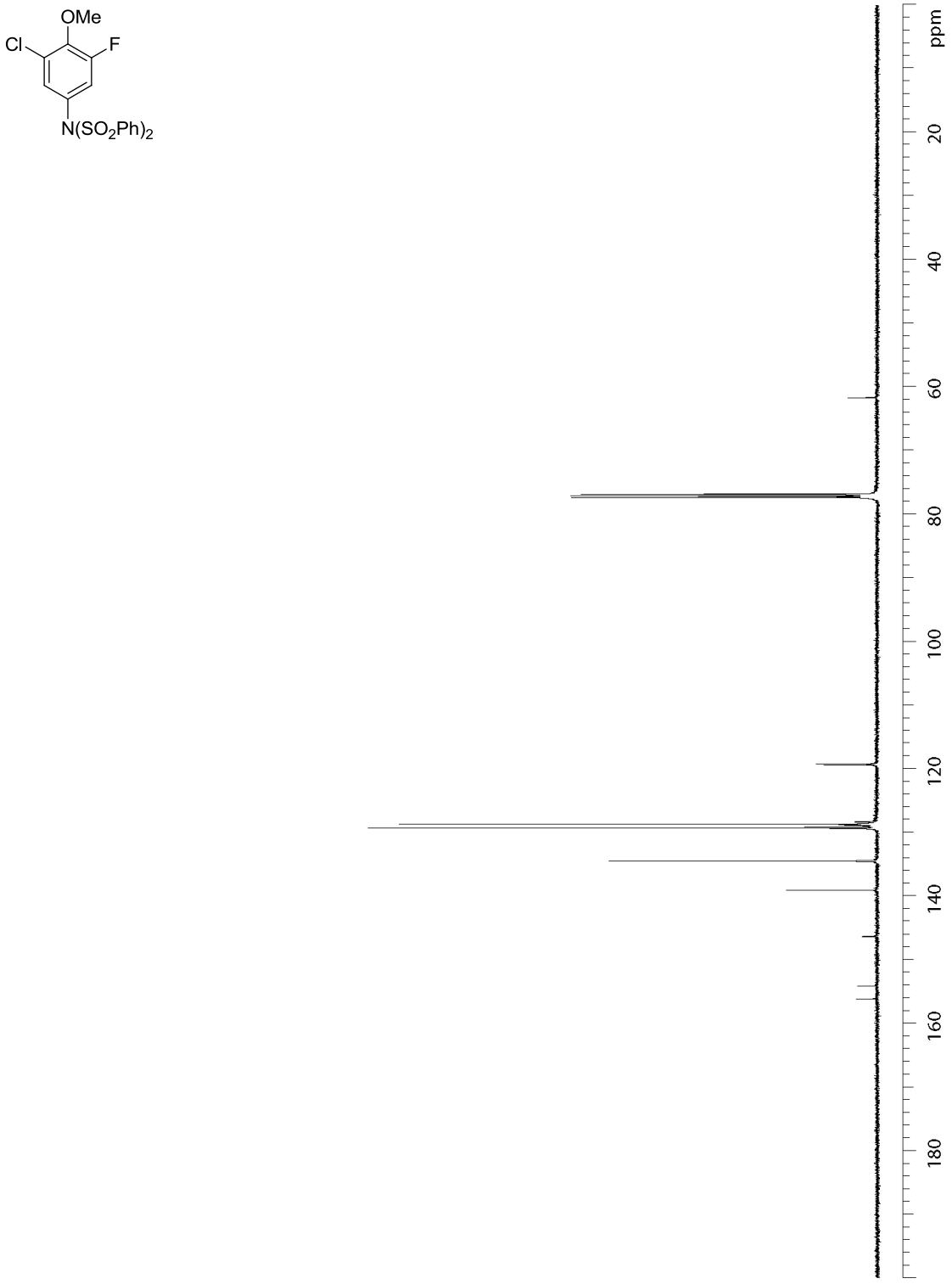

**2j-II**



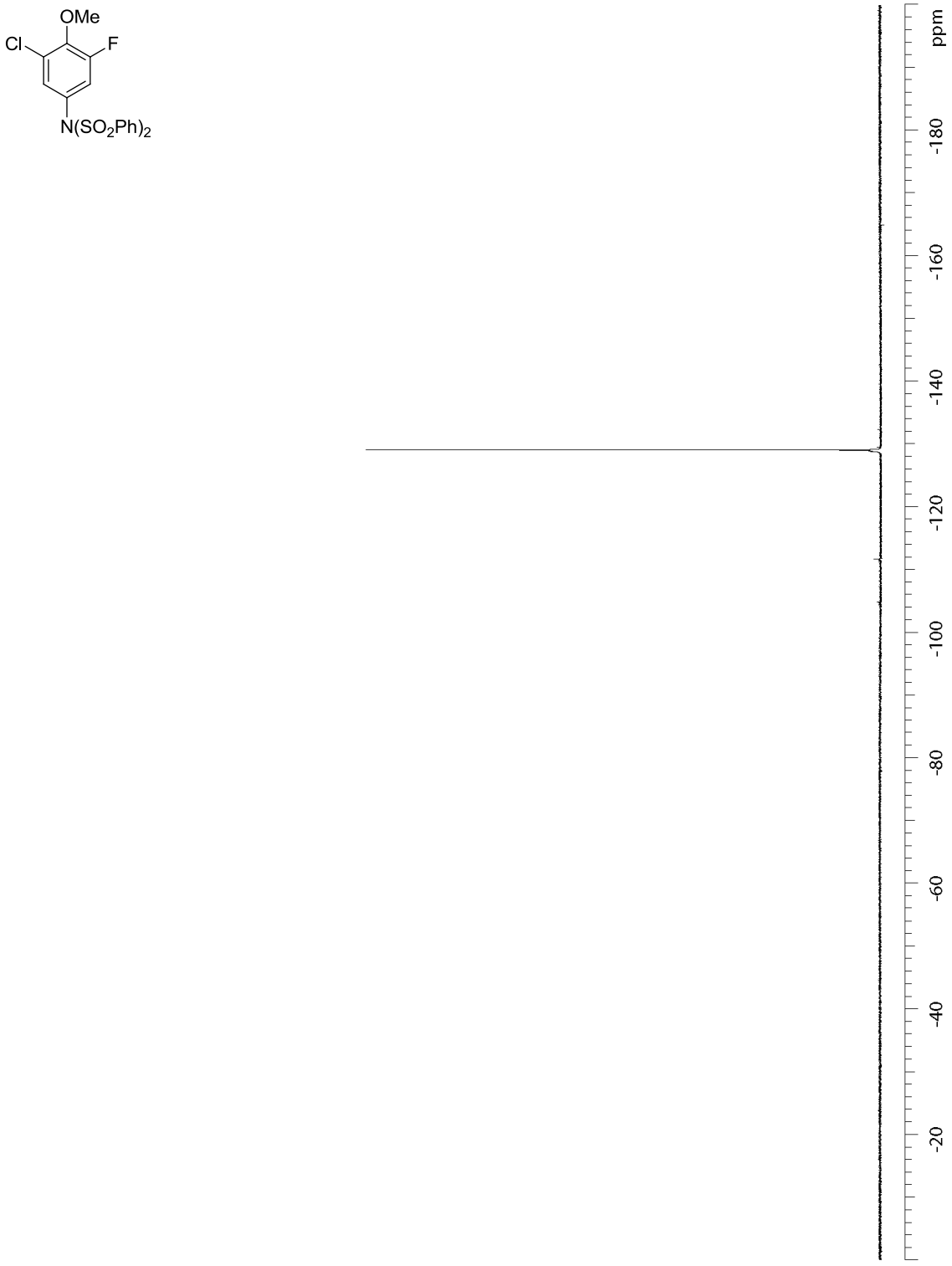
$^1$H NMR ($CDCl_3$, 23 ºC) of **2k**



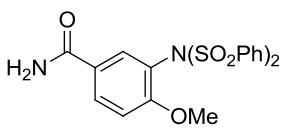
$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2k**

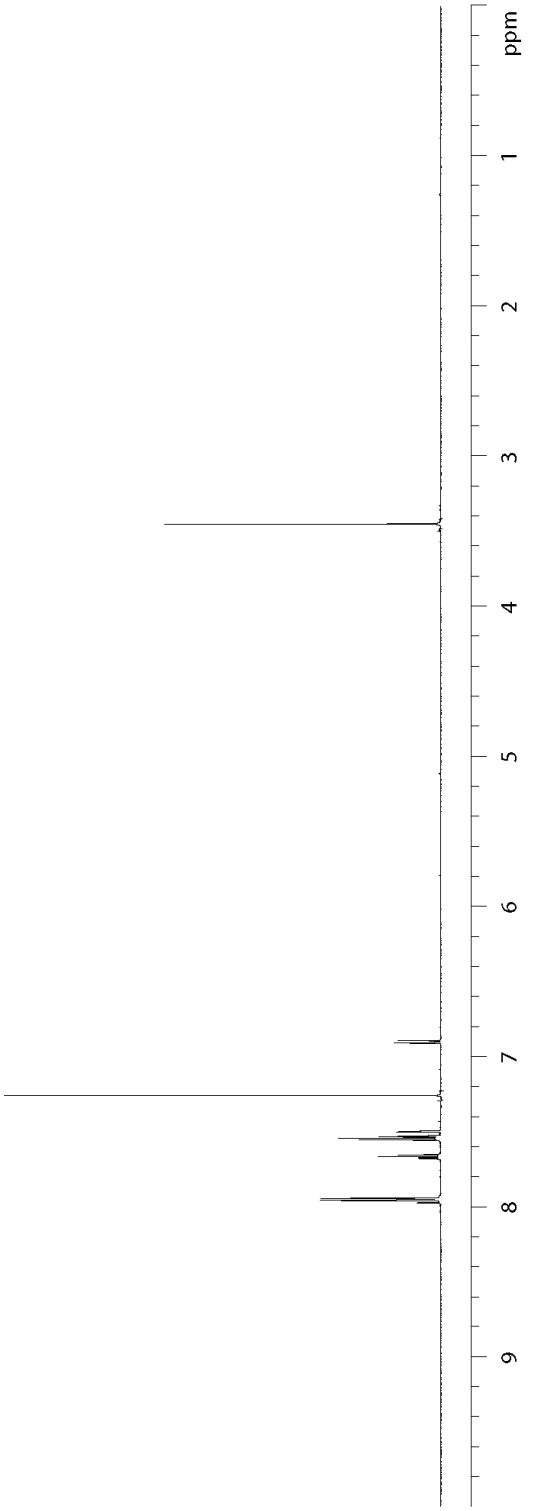


$^{19}F$ NMR ($CDCl_3$, 23 ºC) of **2k**

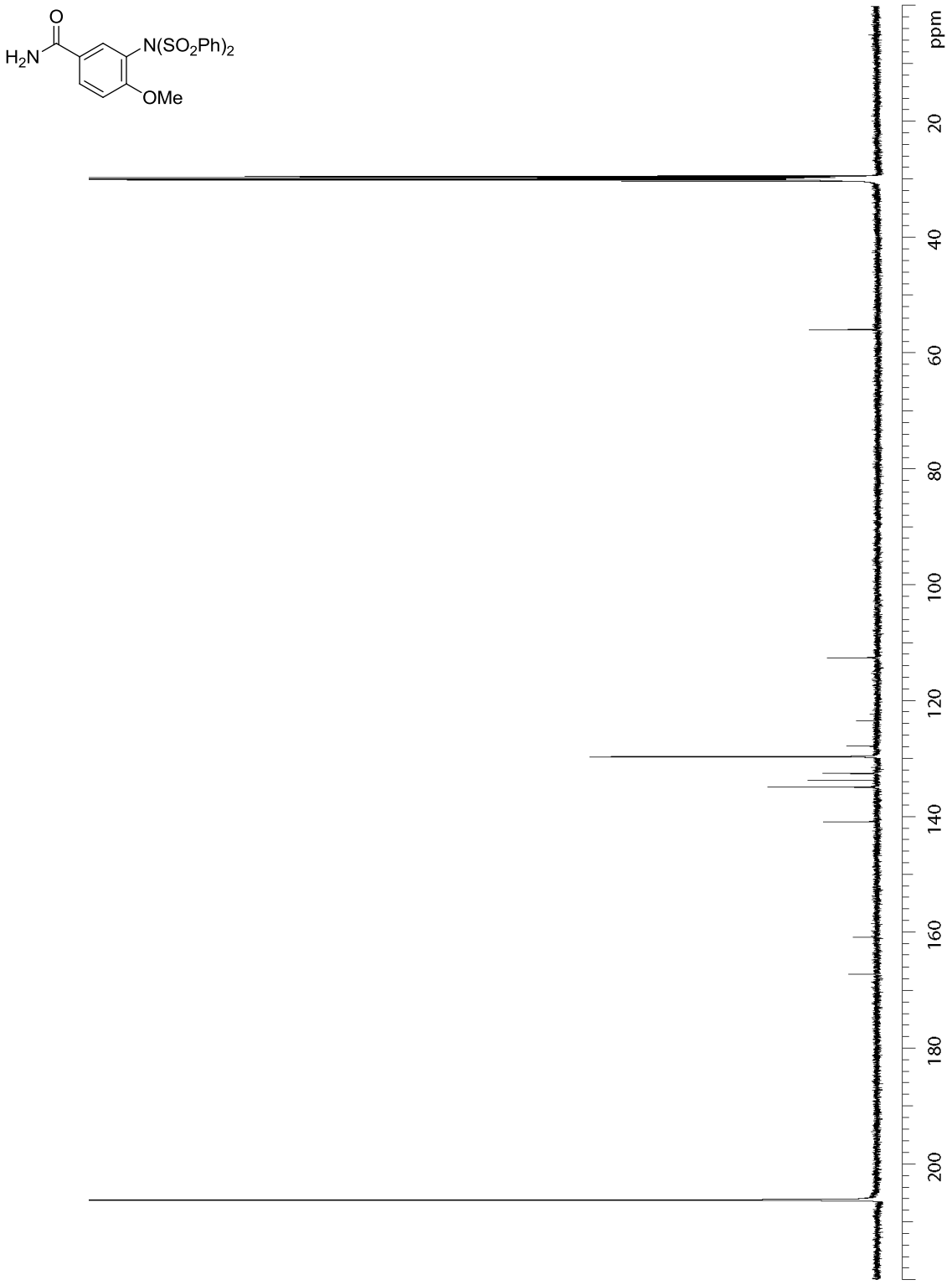


$^1$H NMR ($CDCl_3$, 23 ºC) of **2l**

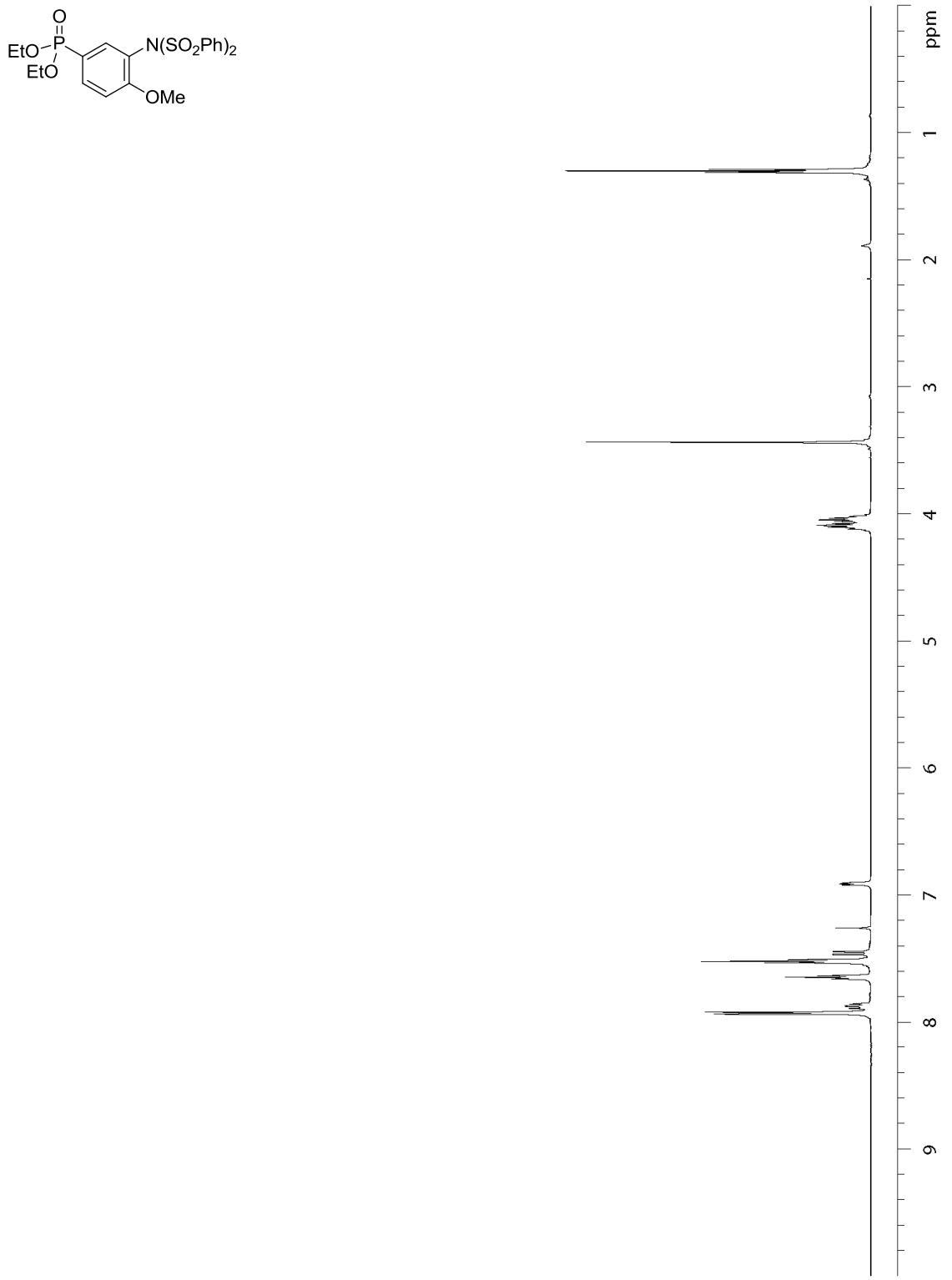


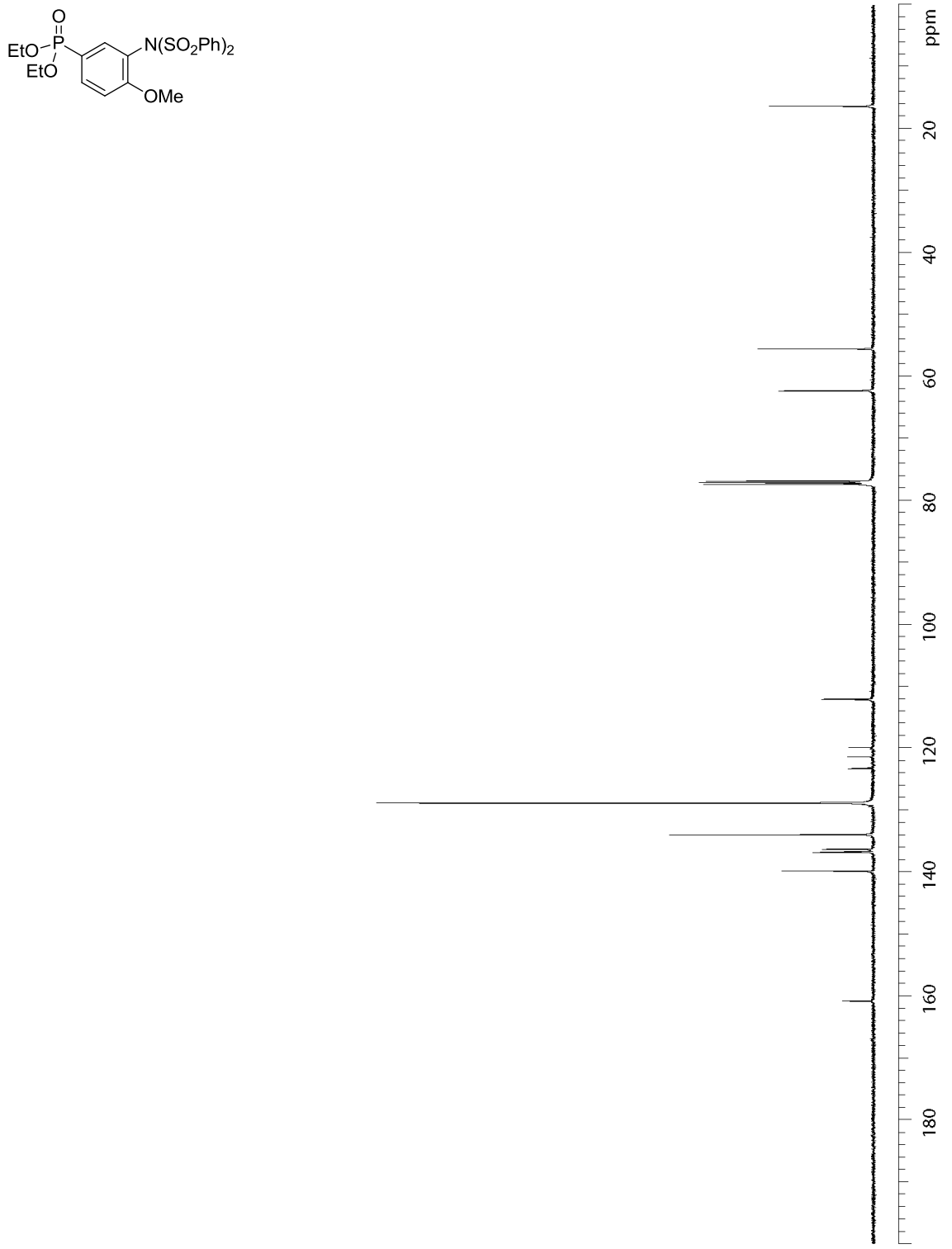
$^{13}$C NMR ($(CD_3)_2CO$, 23 ºC) of **2l**



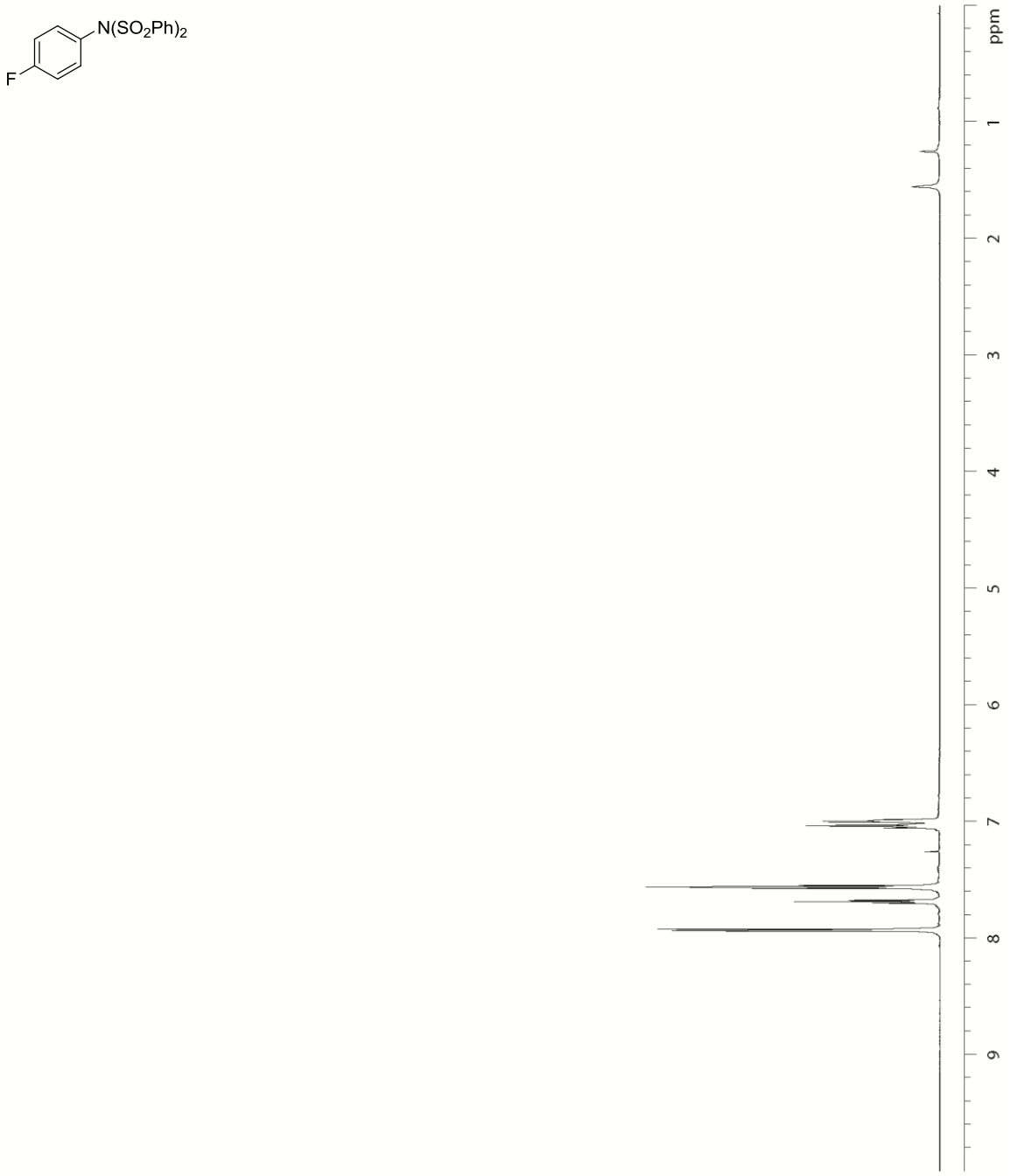
$^1$H NMR ($CDCl_3$, 23 ºC) of **2m**



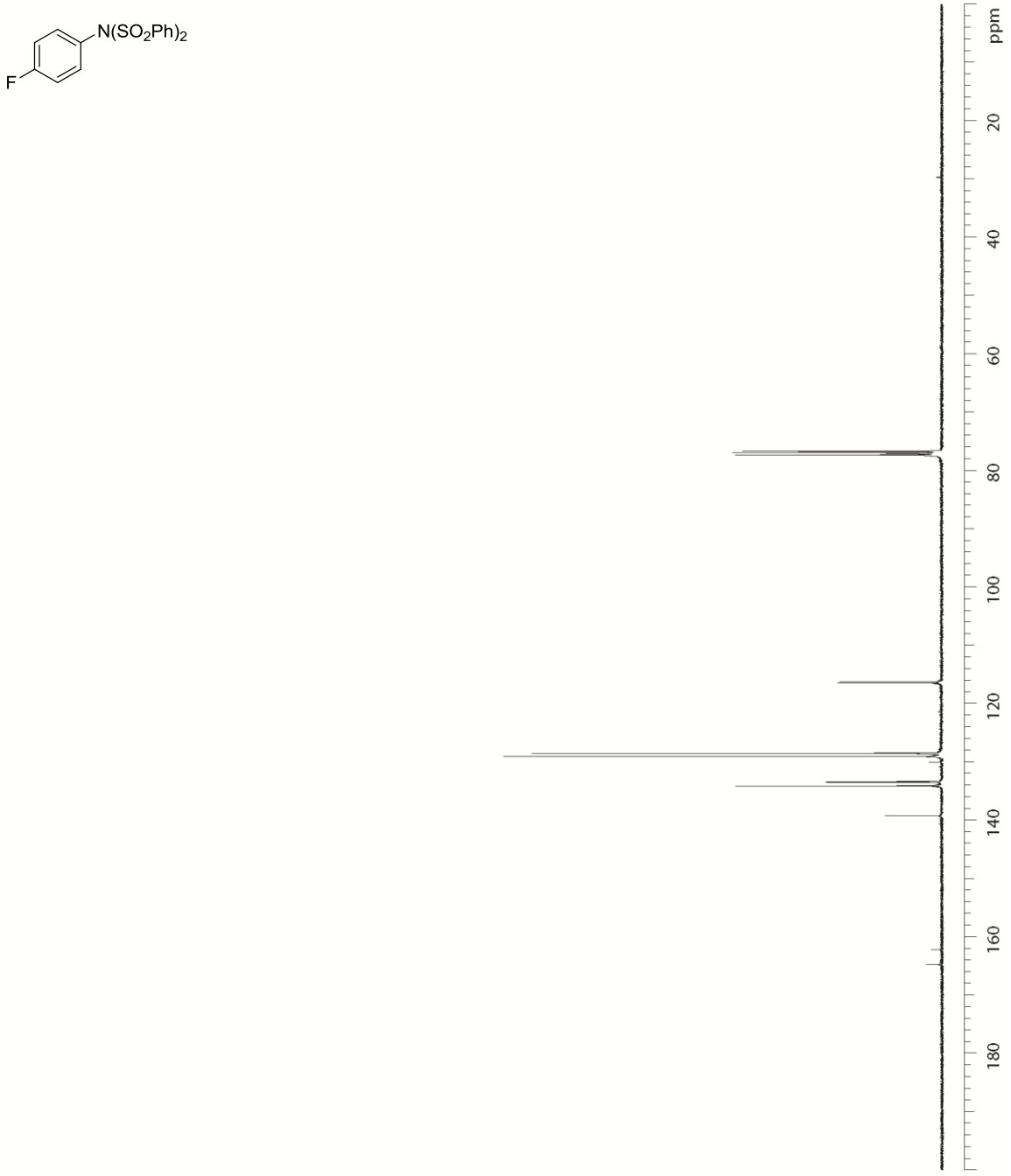
$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2m**



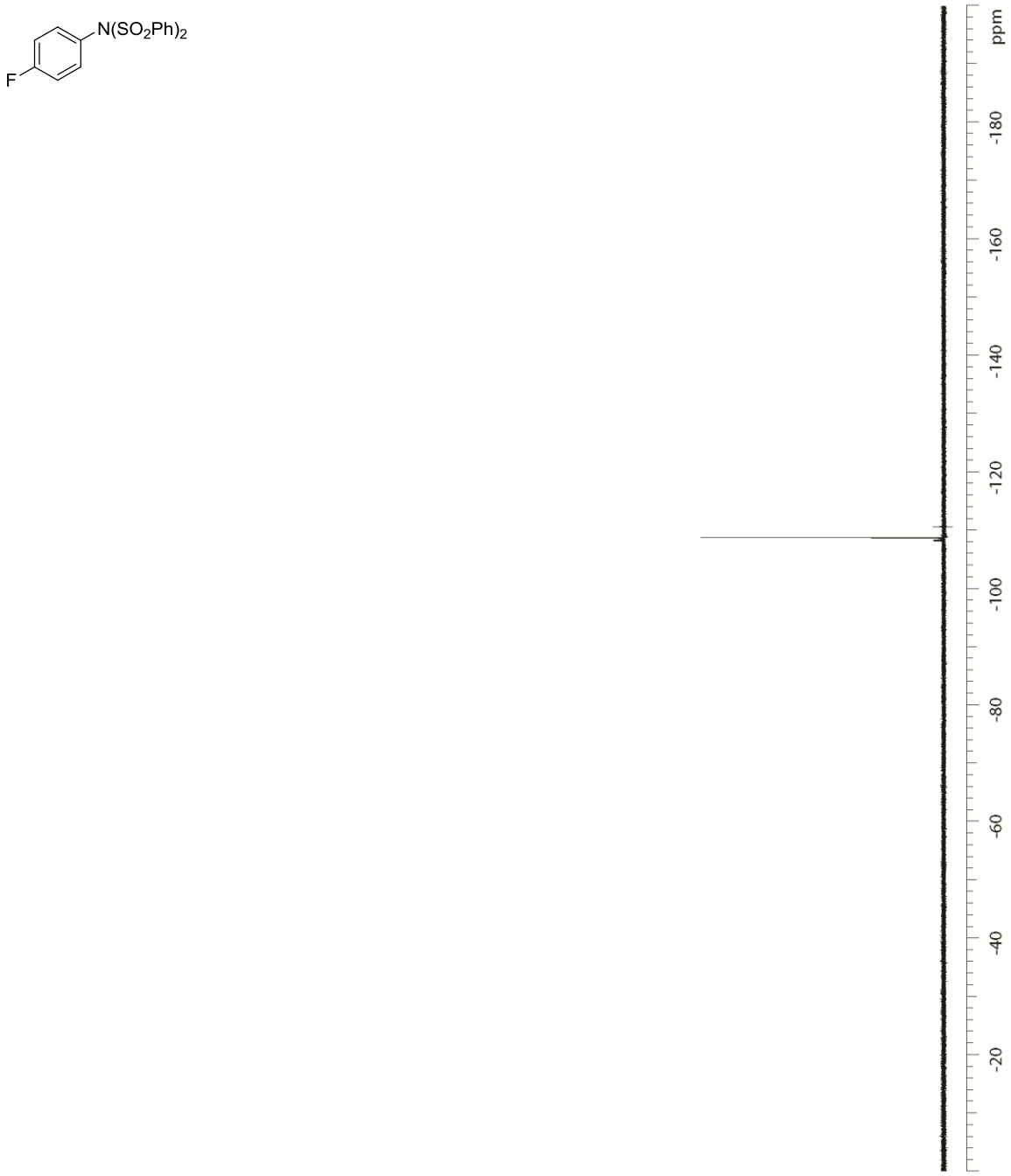
$^1$H NMR ($CDCl_3$, 23 ºC) of **2n**



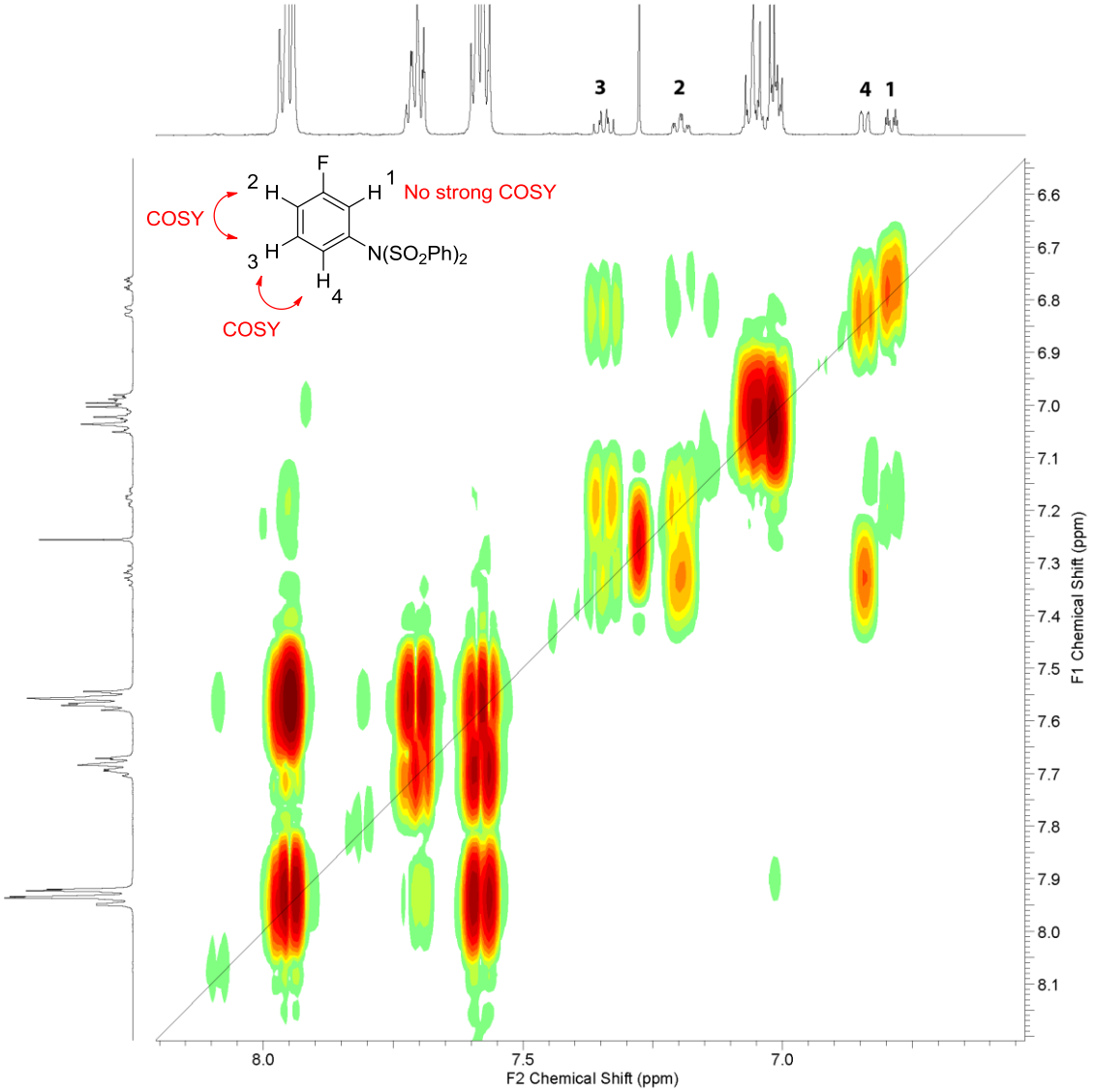
$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2n**



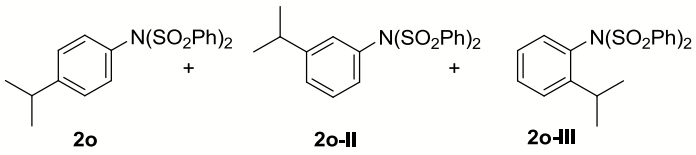
$^{19}$F NMR ($CDCl_3$, 23 ºC) of **2n**



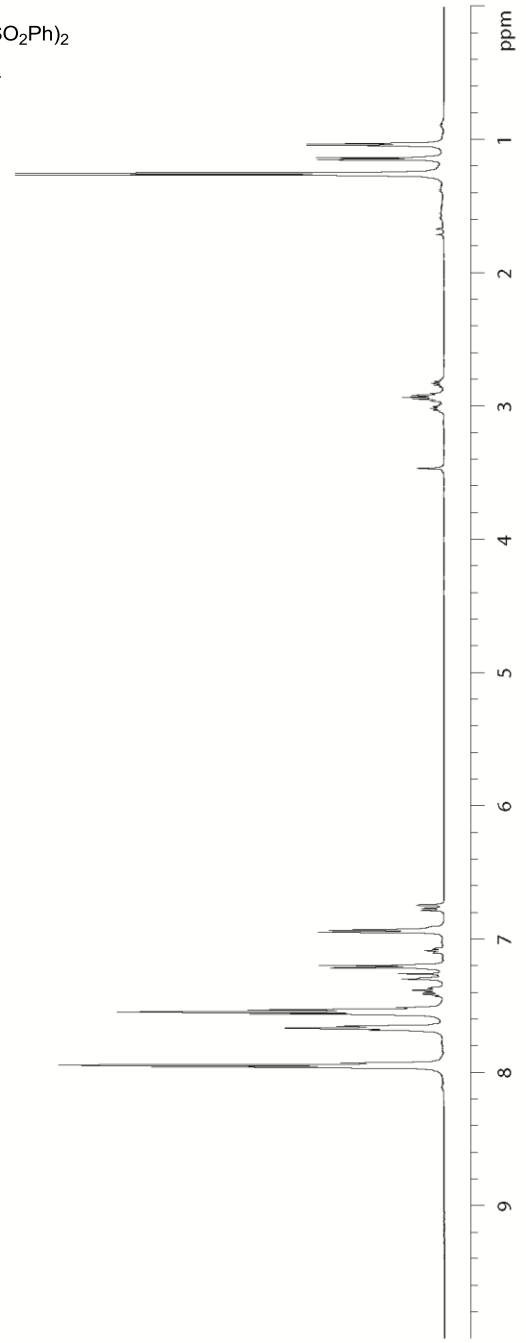
Assignment of **2n-II**



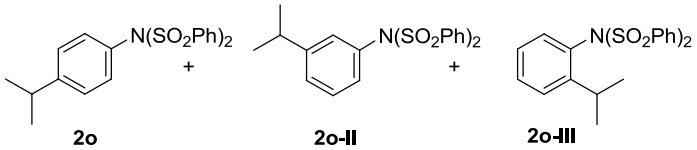
$^1$H NMR ($CDCl_3$, 23 ºC) of **2o**



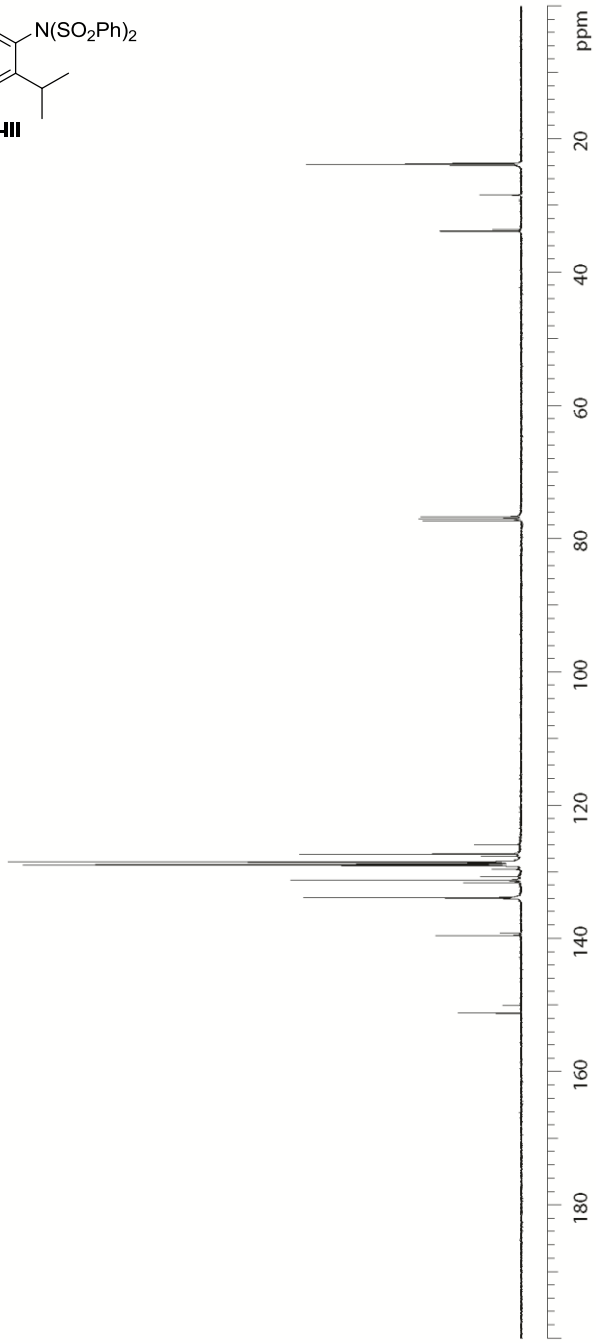

**2o** **2o-II** **2o-III**



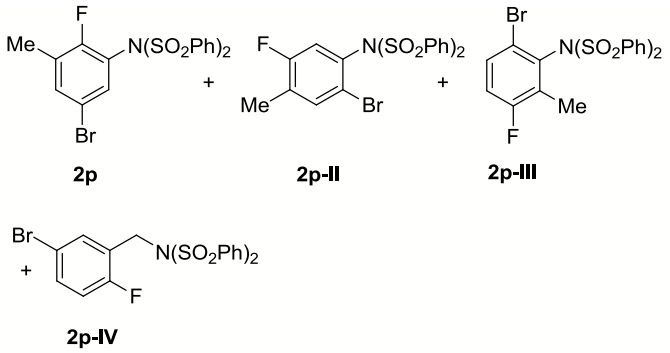
$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2o**




**2o** **2o-II** **2o-III**



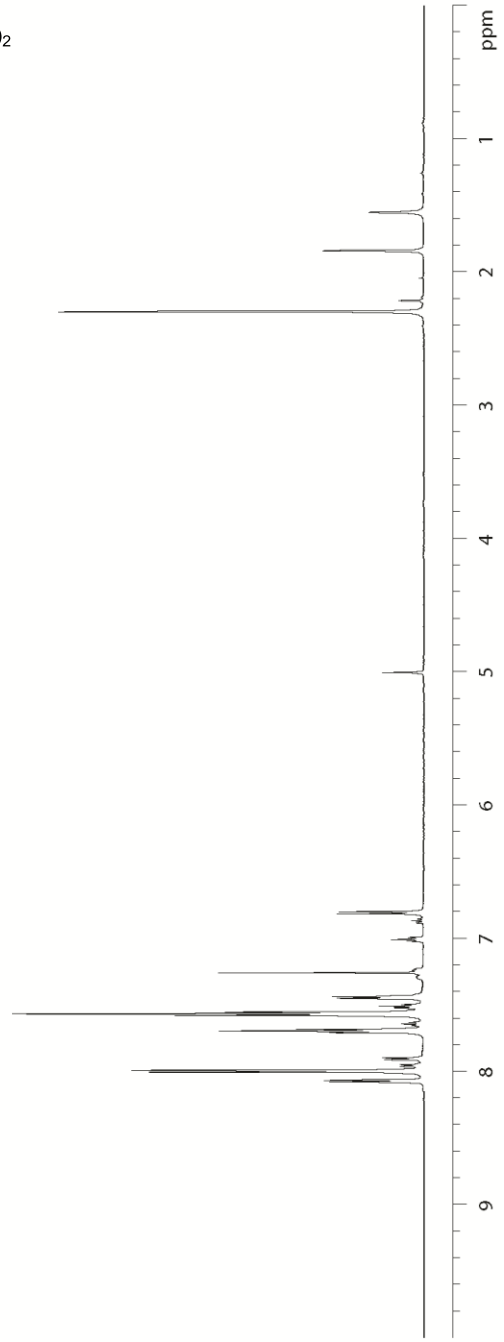
$^1$H NMR ($CDCl_3$, 23 ºC) of **2p**, **2p-II**, **2p-III**, and **2p-IV**



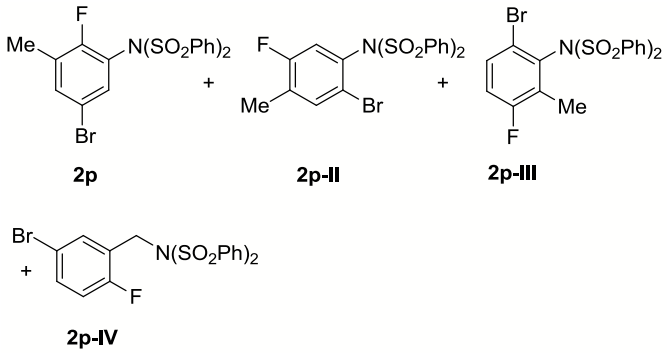

**2p** **2p-II** **2p-III**




**2p-IV**



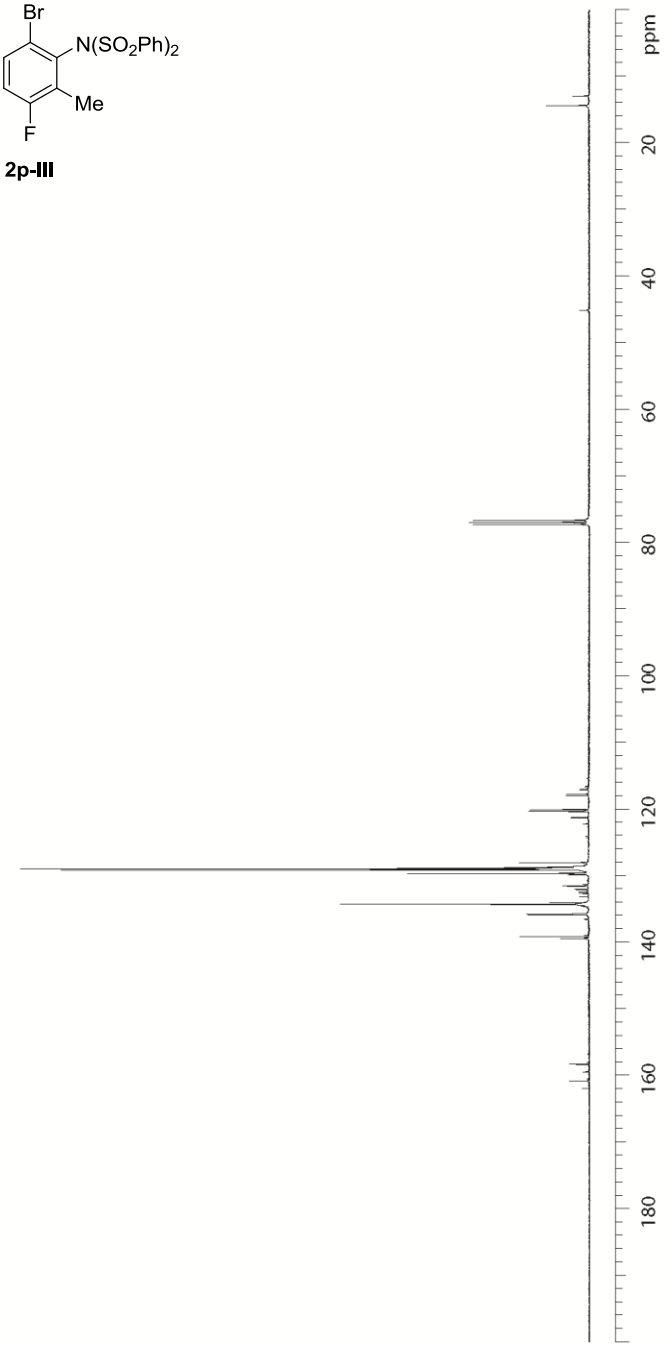
$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2p**, **2p-II**, **2p-III**, and **2p-IV**



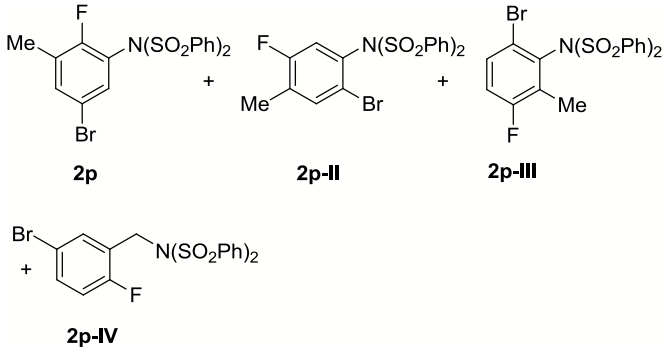

**2p** **2p-II** **2p-III**




**2p-IV**



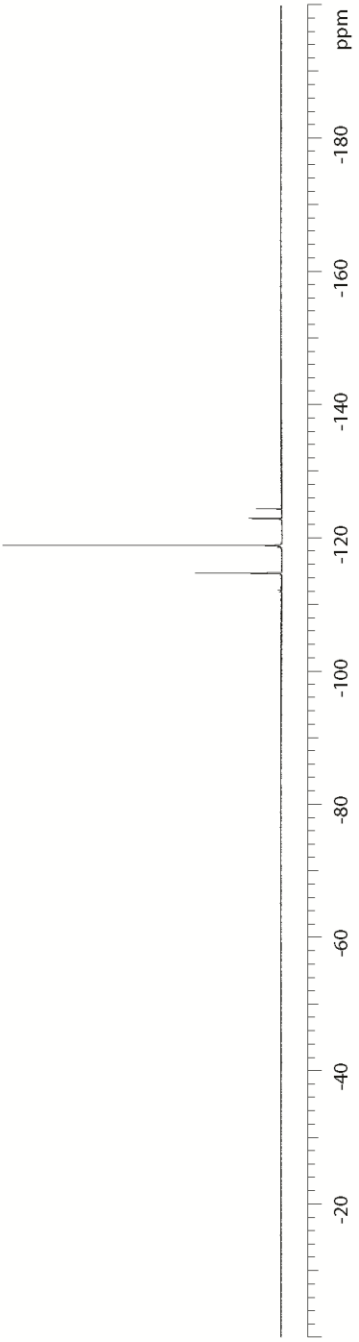
$^{19}$F NMR ($CDCl_3$, 23 ºC) of **2p**, **2p-II**, **2p-III**, and **2p-IV**




**2p** **2p-II** **2p-III**

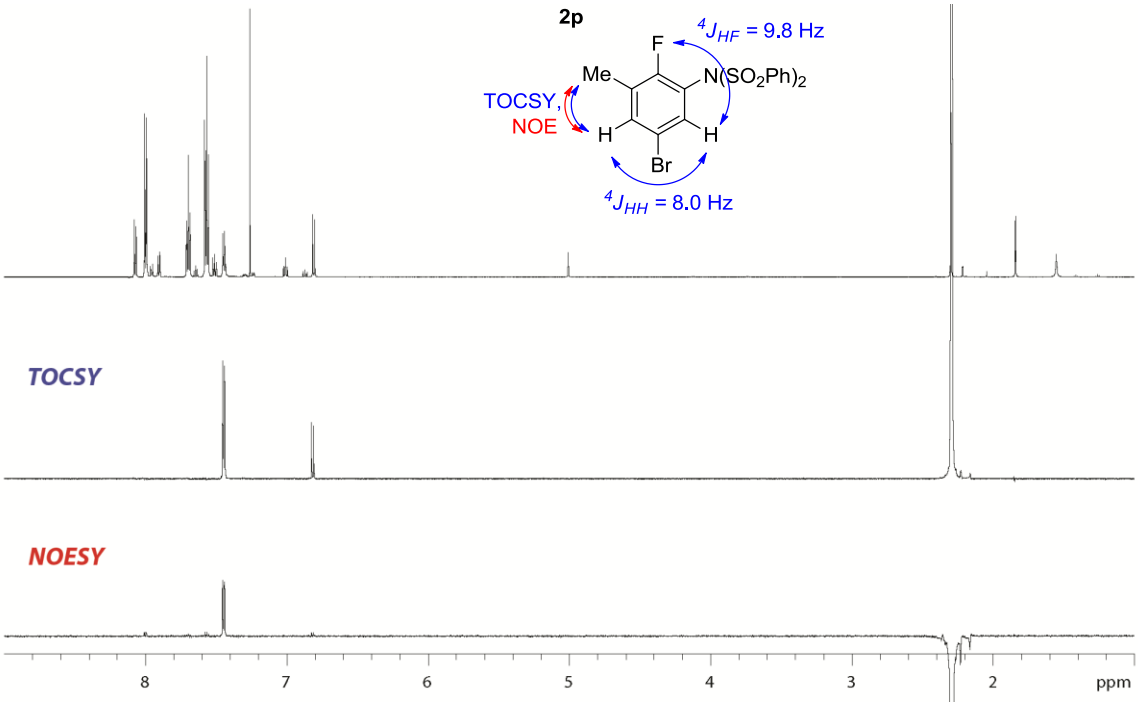



**2p-IV**

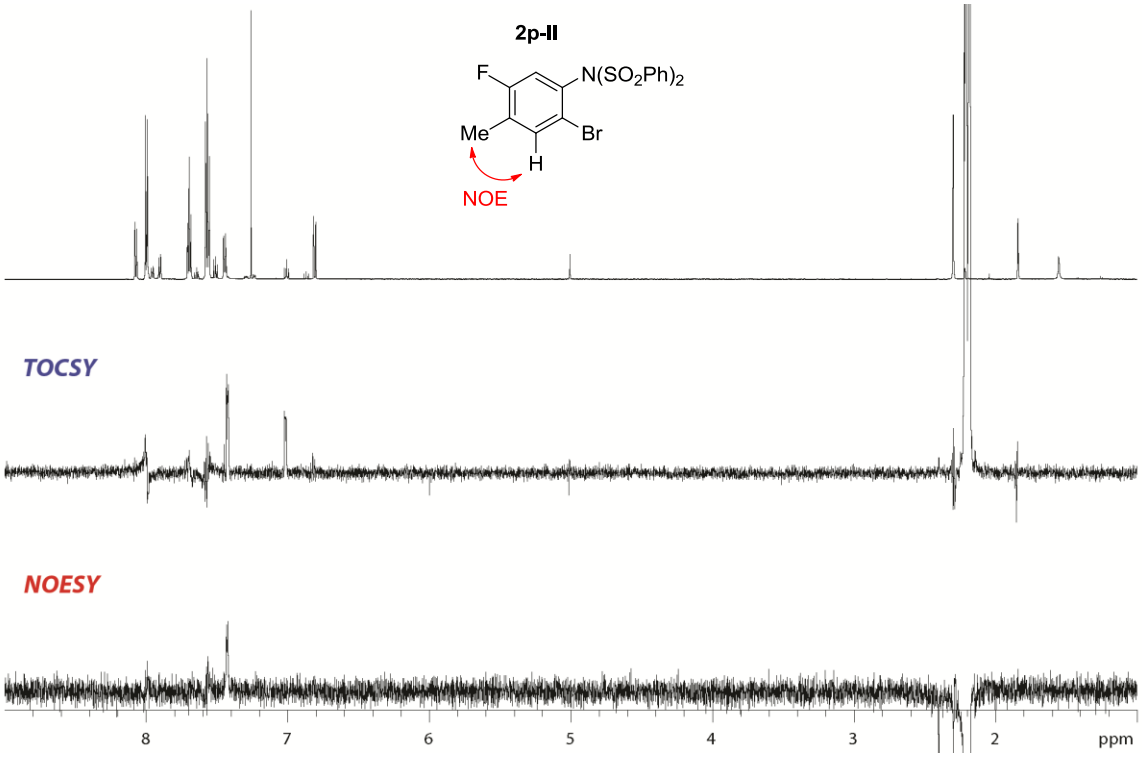


Assignment of the products **2p, 2p-II, 2p-III, and 2p-IV**

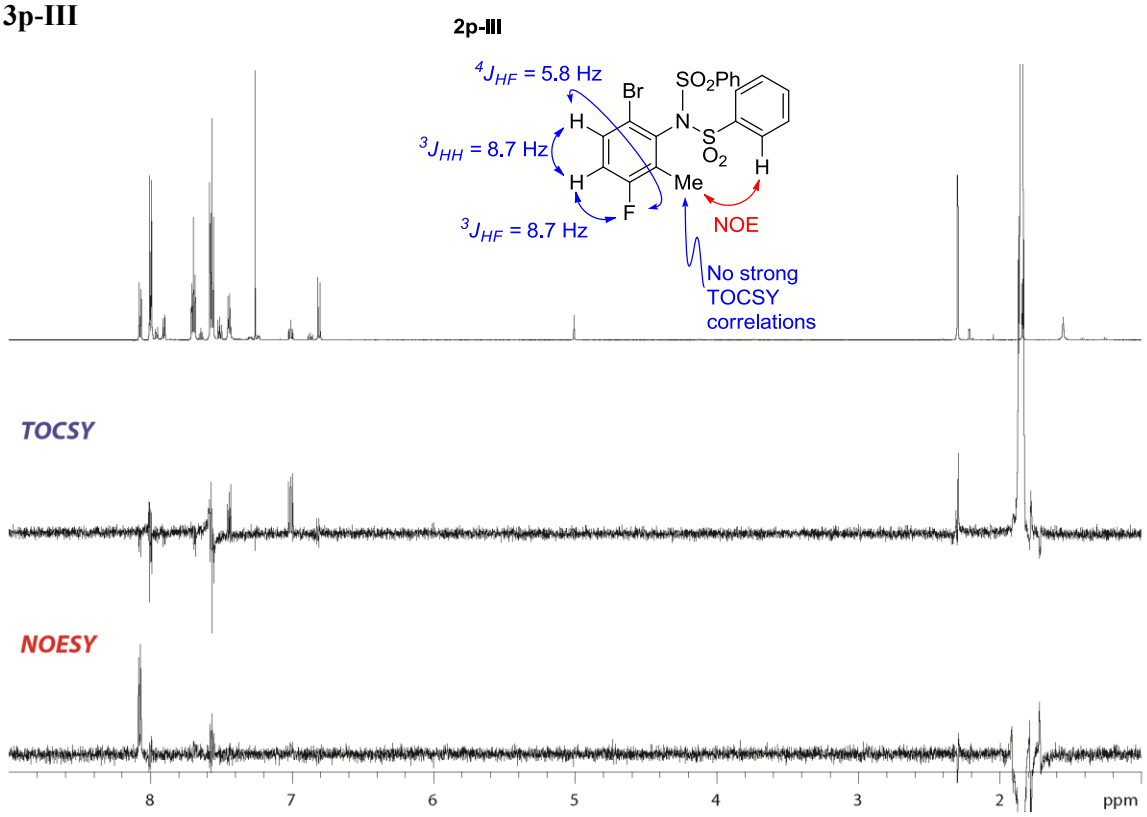
**2p**



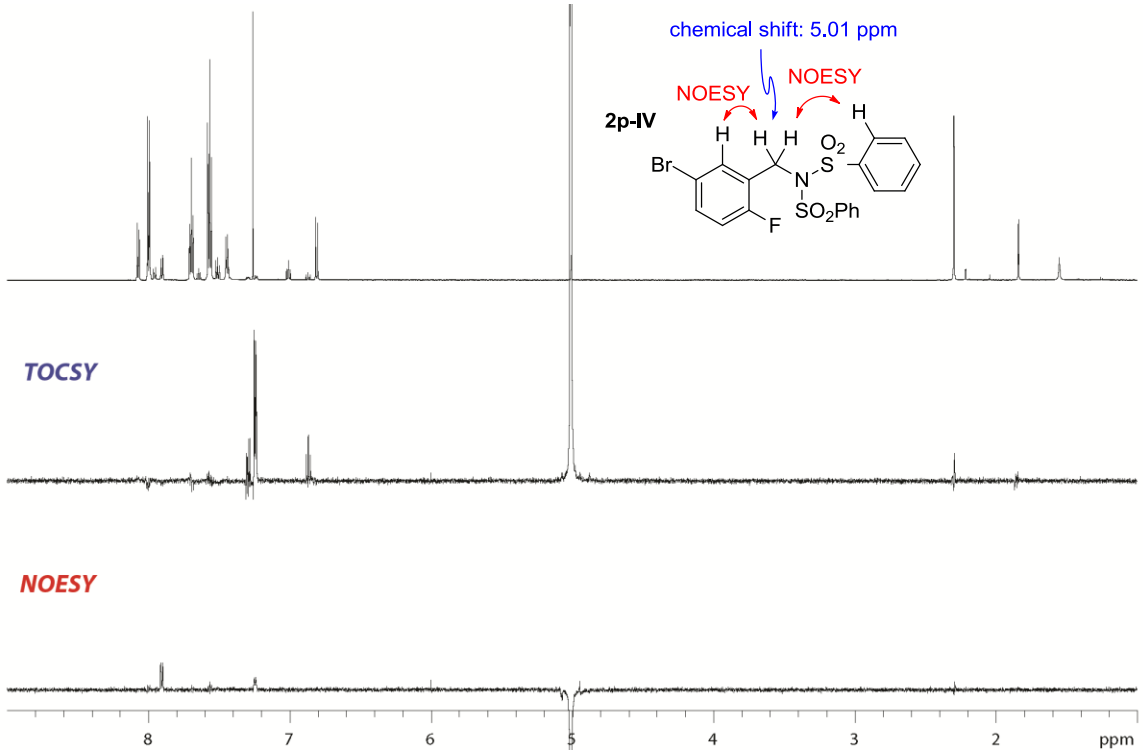

**2p-II**



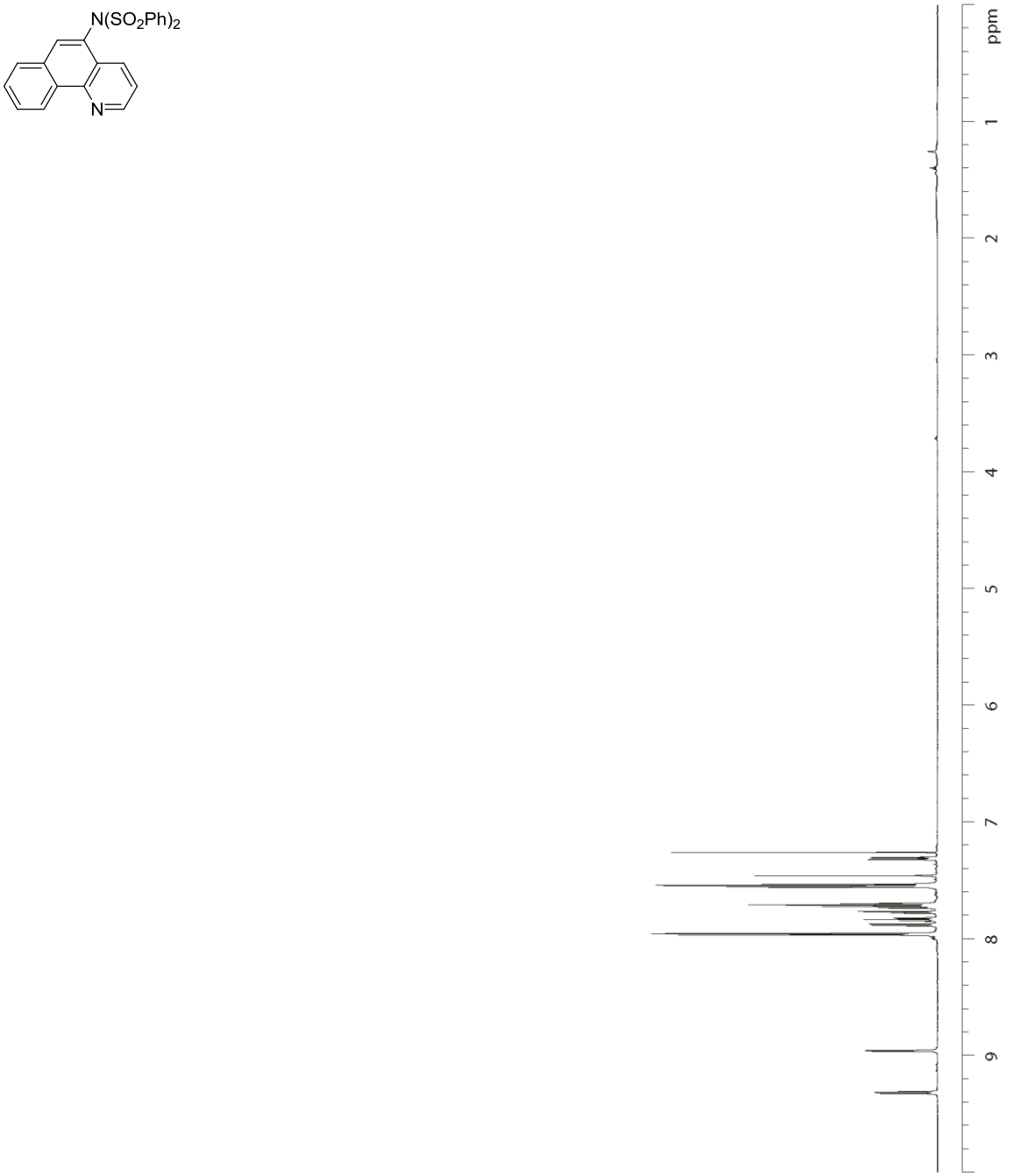
**3p-III**


2p-III
$^4J_{HF}$ = 5.8 Hz
$^3J_{HH}$ = 8.7 Hz
$^3J_{HF}$ = 8.7 Hz
Br
SO2Ph
N
S
O2
H
Me
F
NOE
No strong TOCSY correlations
TOCSY
NOESY
8
7
6
5
4
3
2
ppm

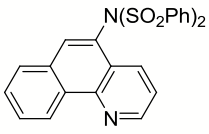
**3p-IV**

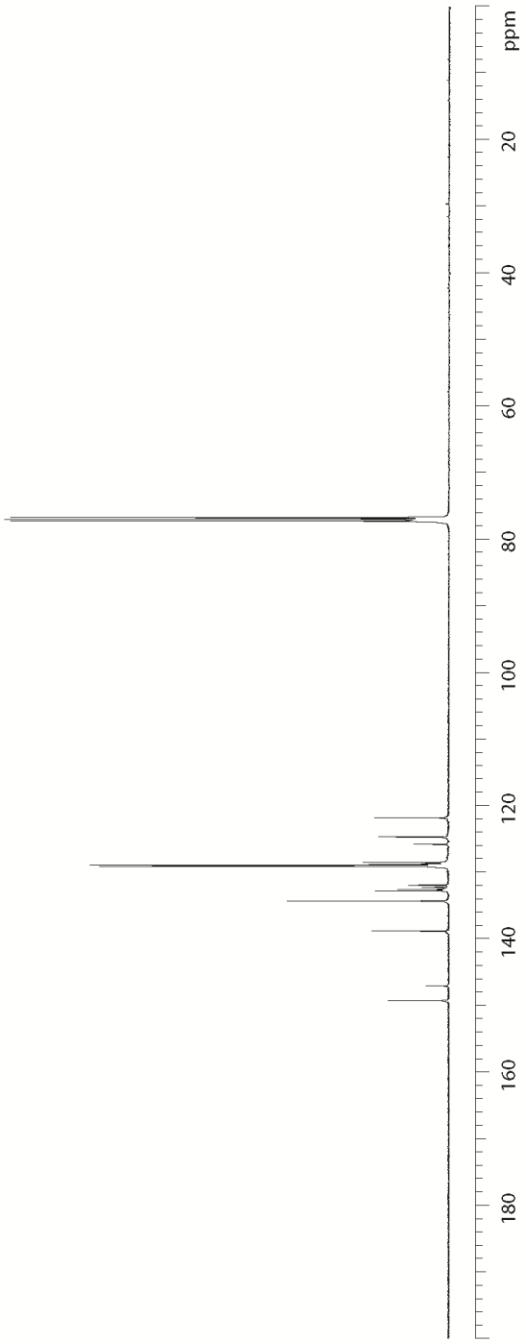

chemical shift: 5.01 ppm
NOESY
NOESY
2p-IV
H
H
H
O2
S
N
Br
F
SO2Ph
TOCSY
NOESY
8
7
6
5
4
3
2
ppm

$^1$H NMR ($CDCl_3$, 23 ºC) of **2q**



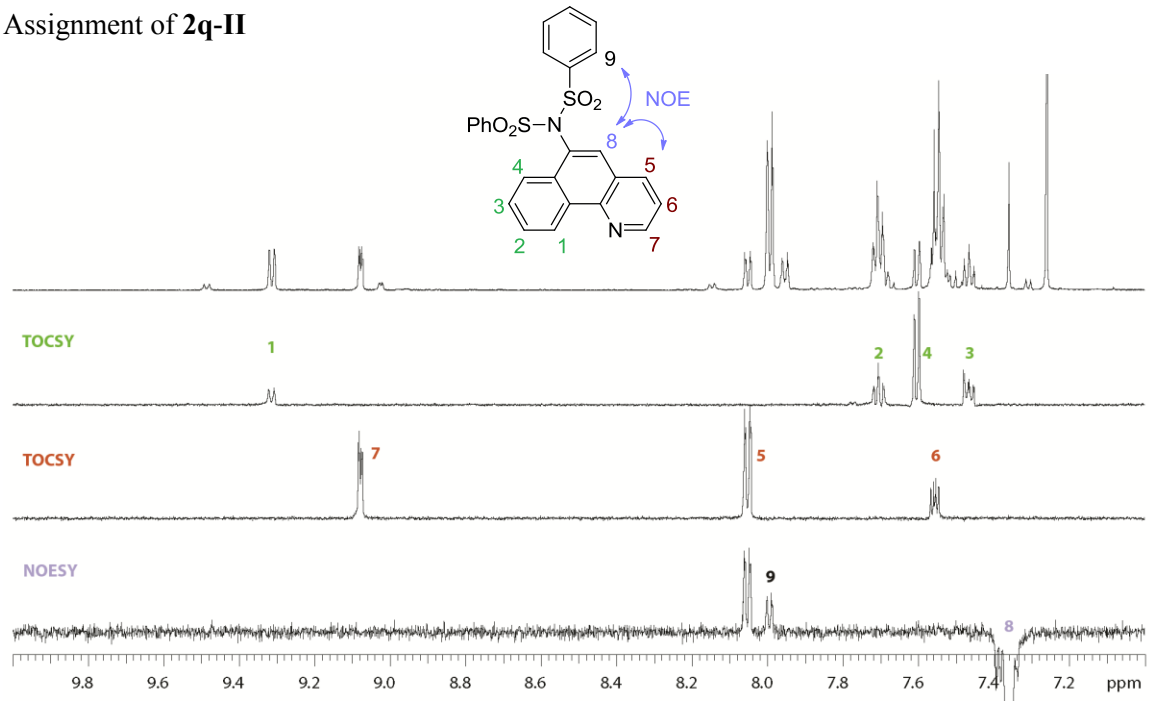
$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2q**



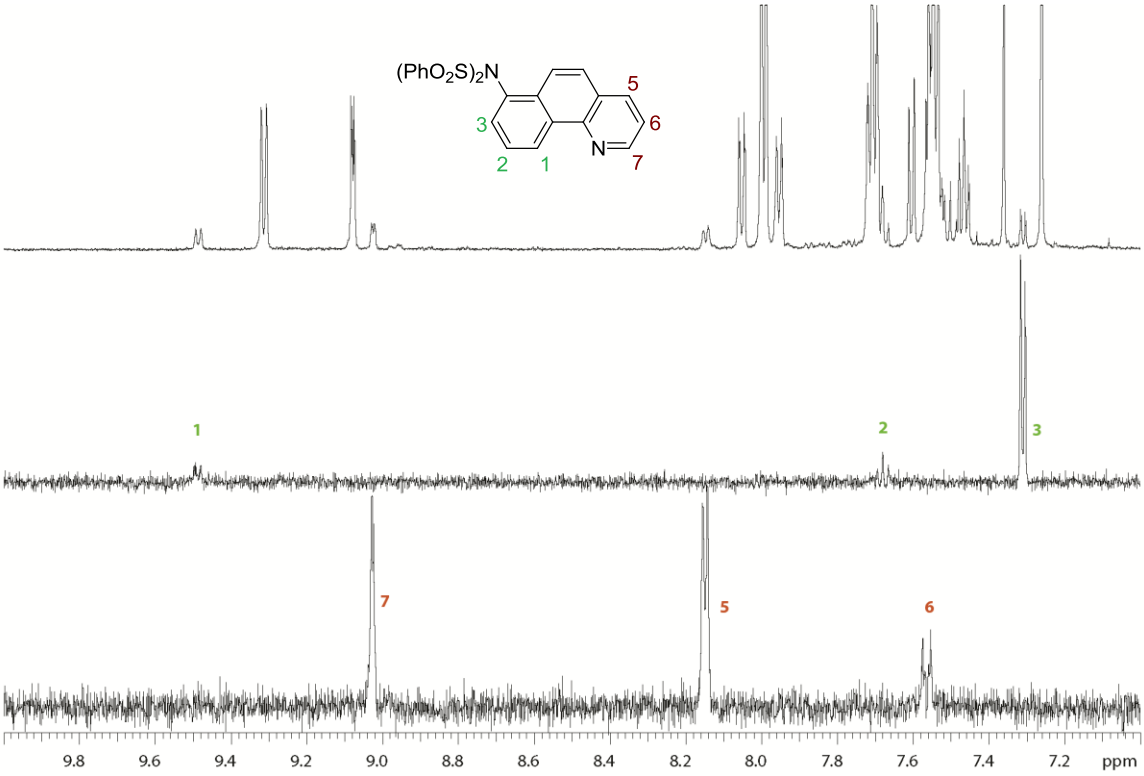



Assignment of the products **2q-II** and **2p-III**

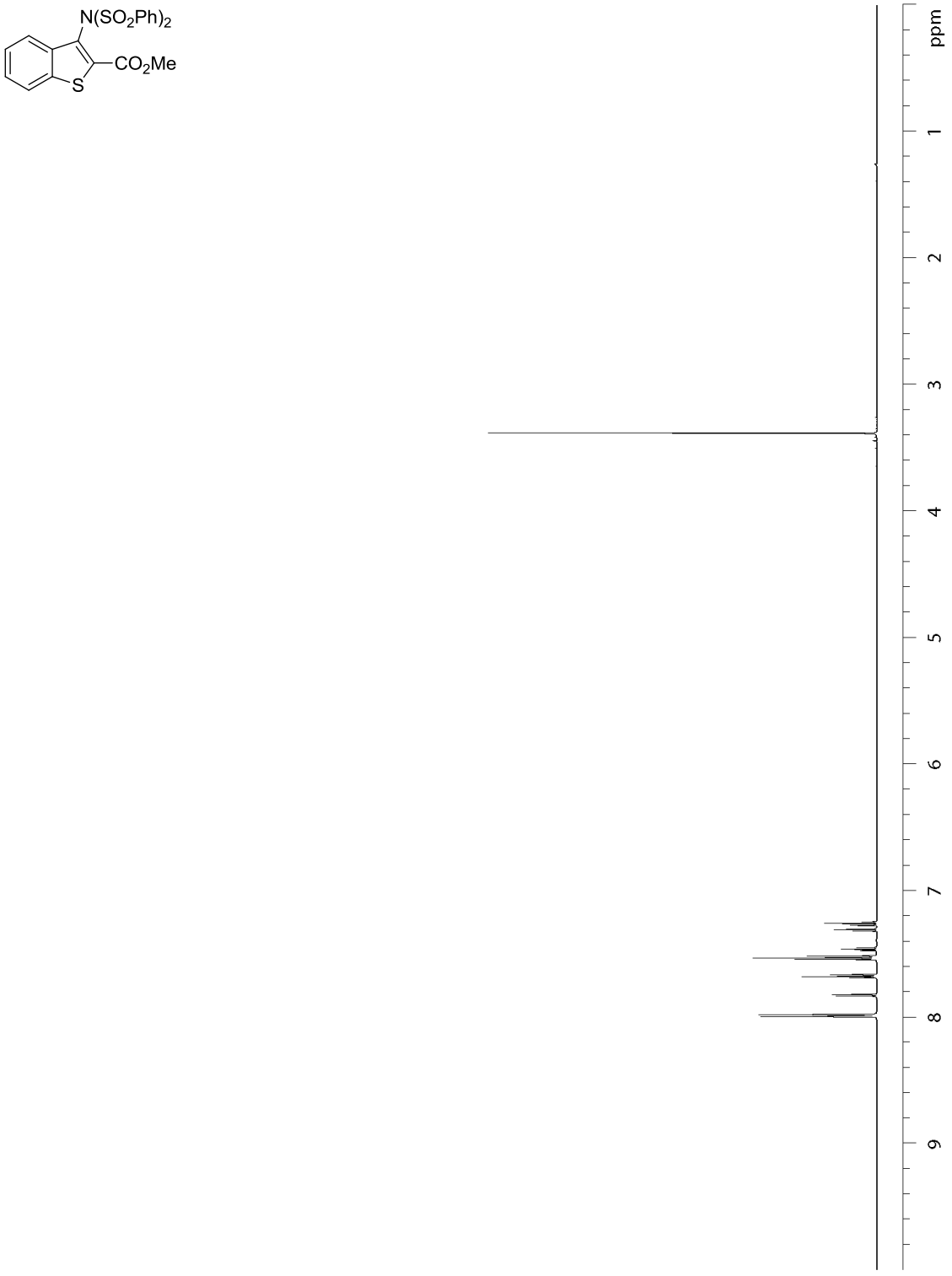
Assignment of **2q-II**



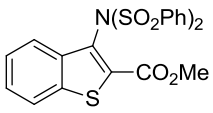

Assignment of **2q-III**

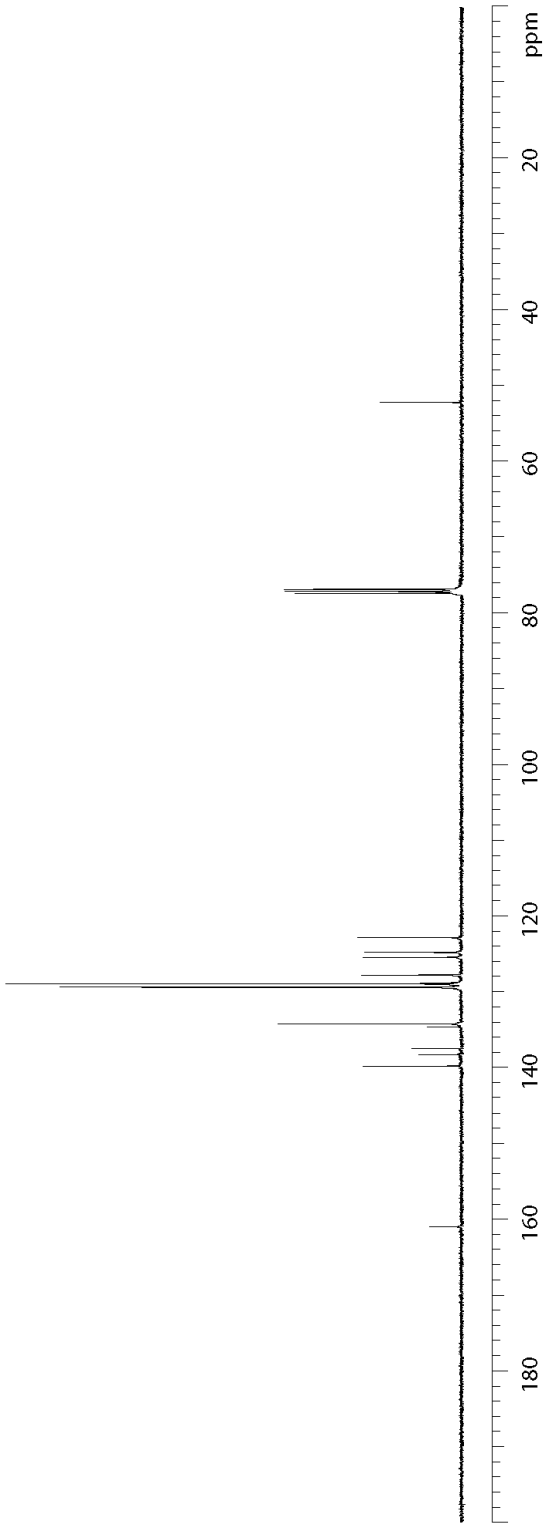


$^1$H NMR ($CDCl_3$, 23 ºC) of **2r**

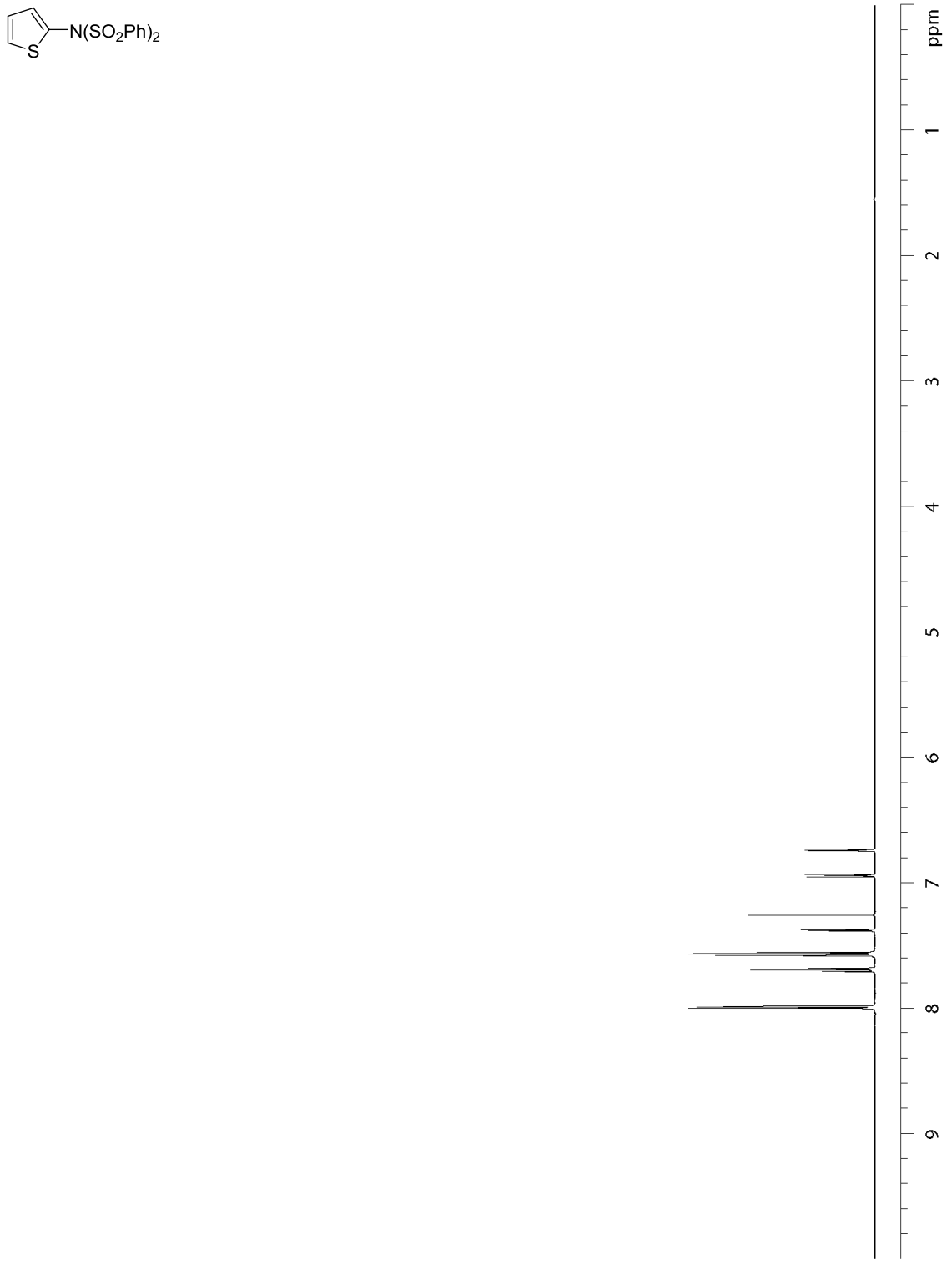


$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2r**

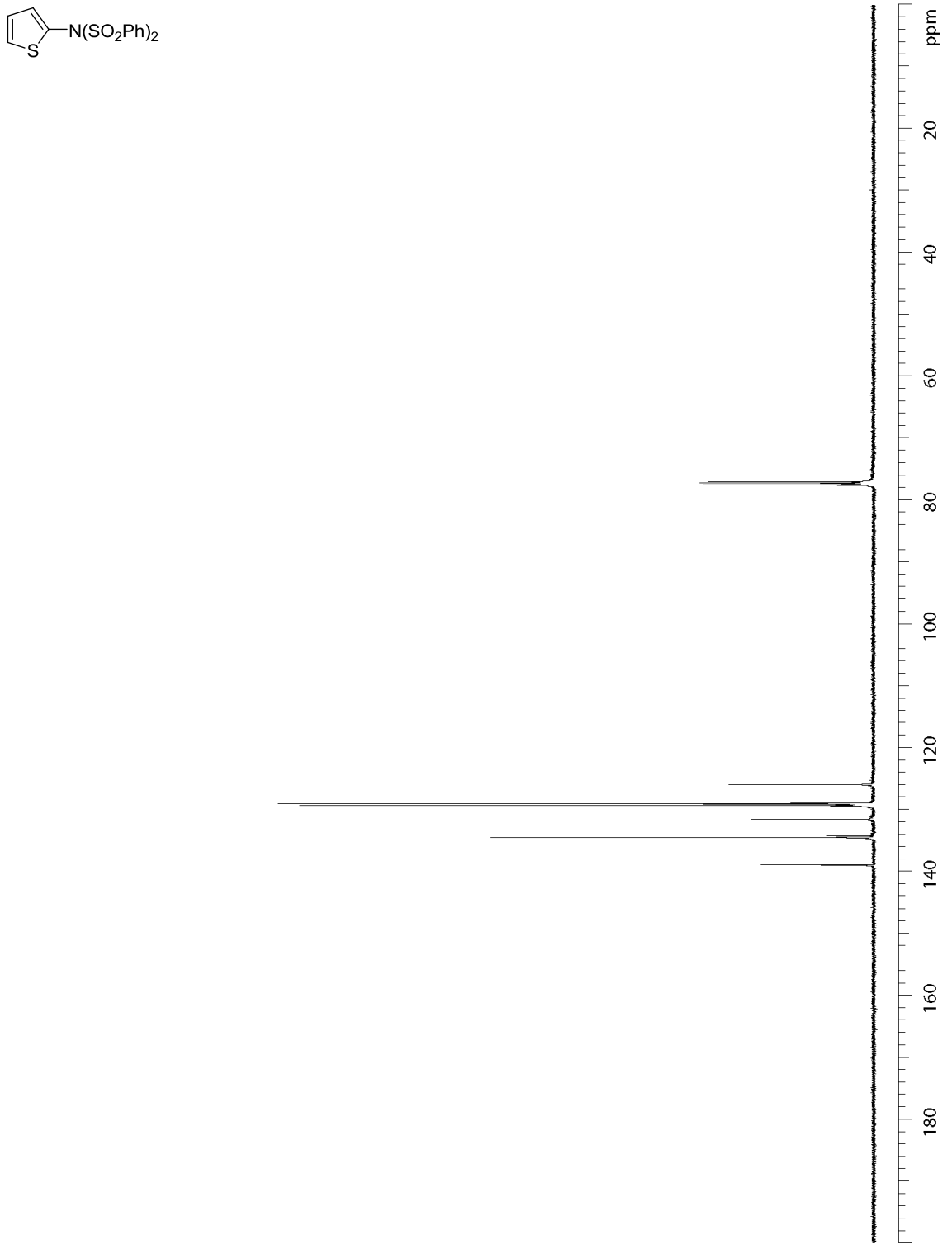


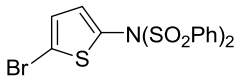
$^1$H NMR ($CDCl_3$, 23 ºC) of **2s**

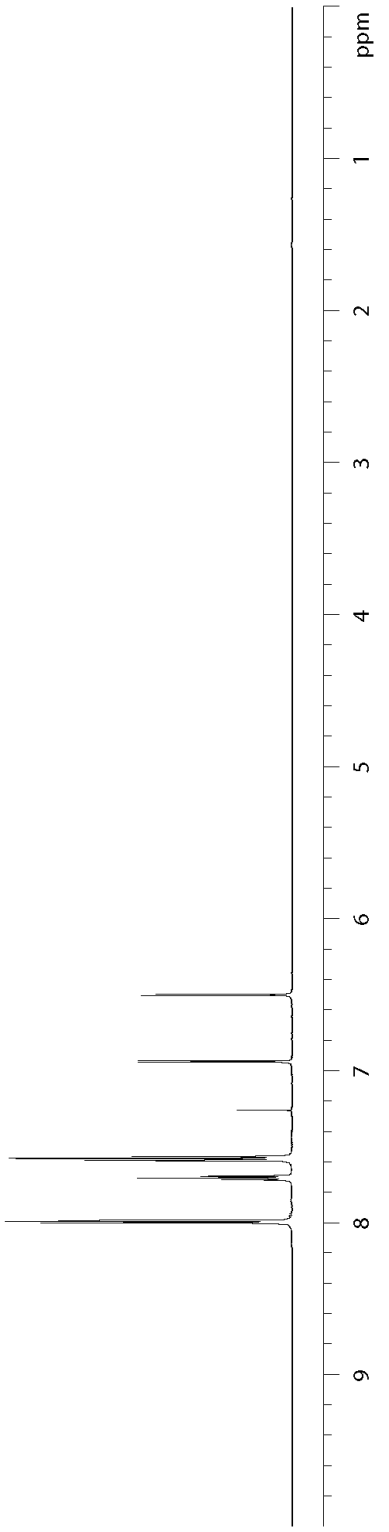


$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2s**

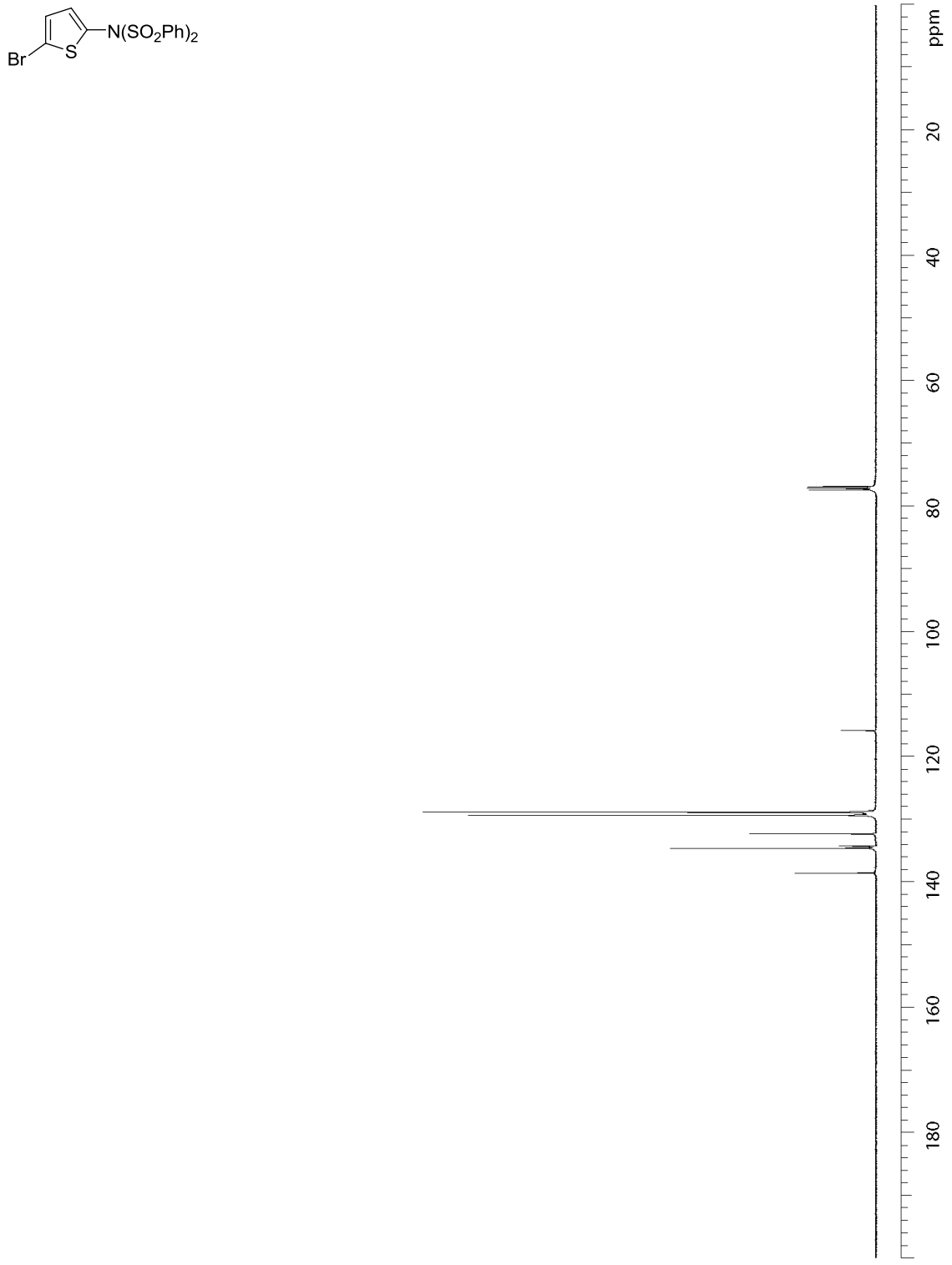


$^1$H NMR ($CDCl_3$, 23 ºC) of **2t**

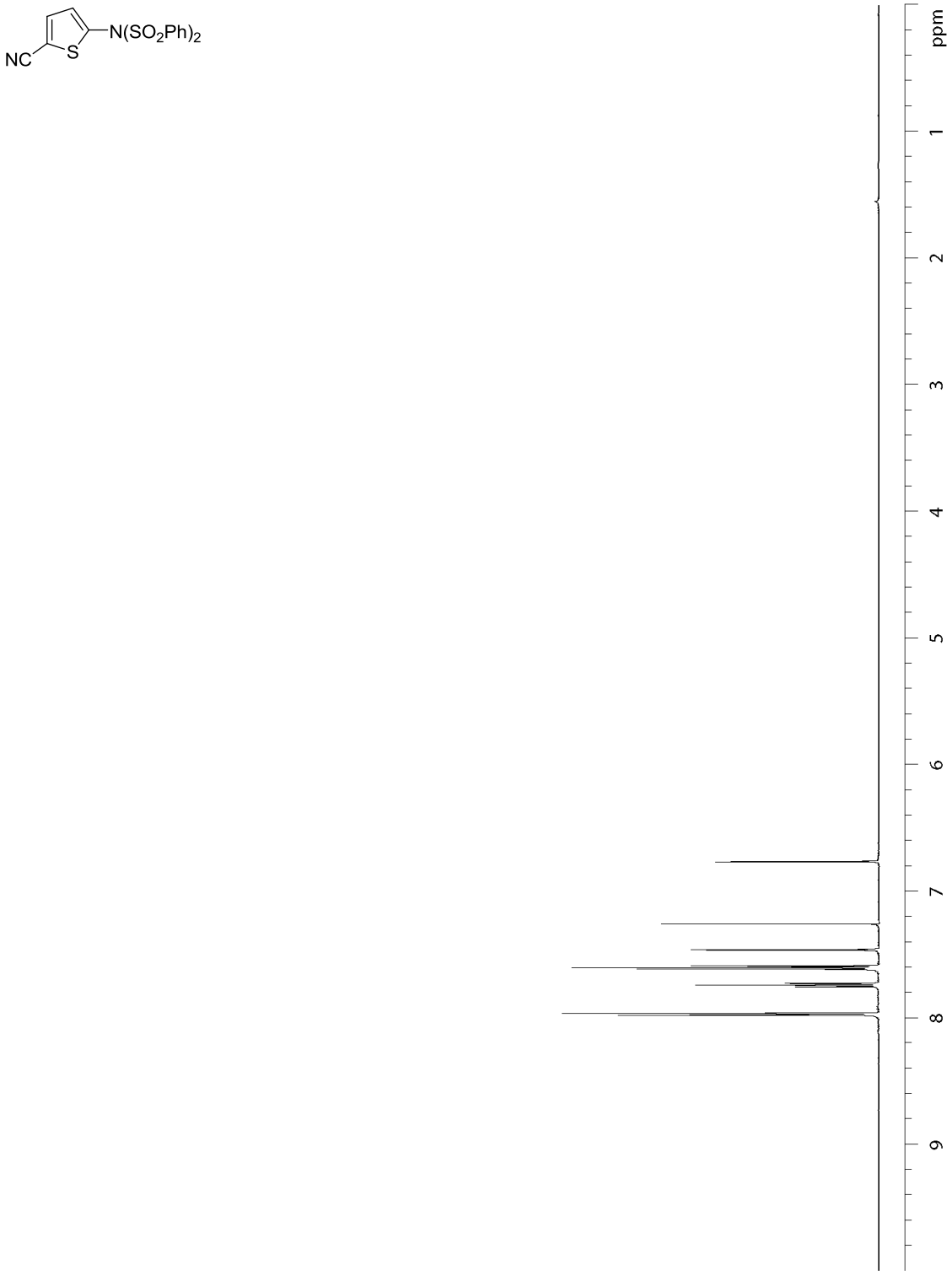


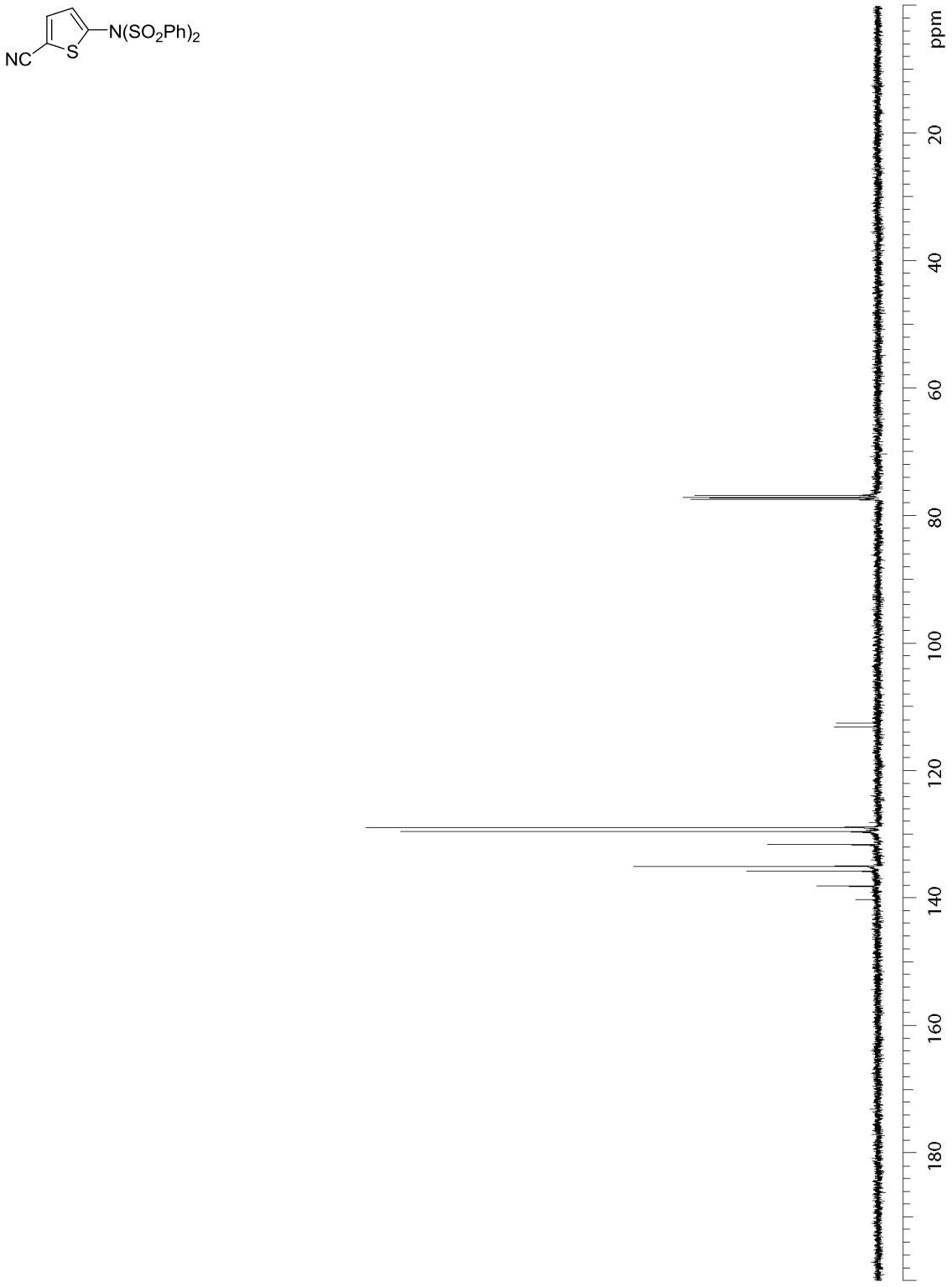
$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2t**



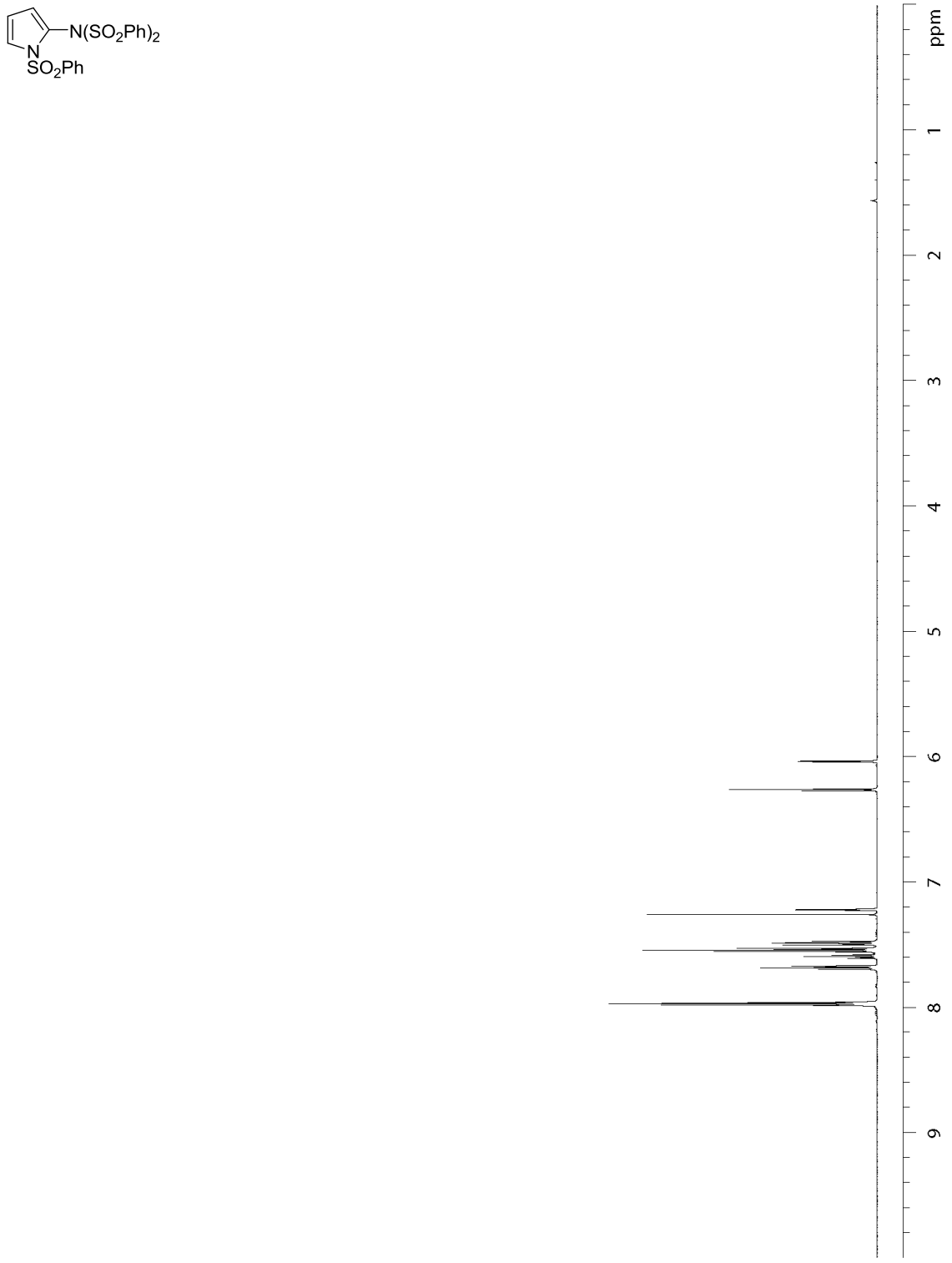
$^1$H NMR ($CDCl_3$, 23 ºC) of **2u**



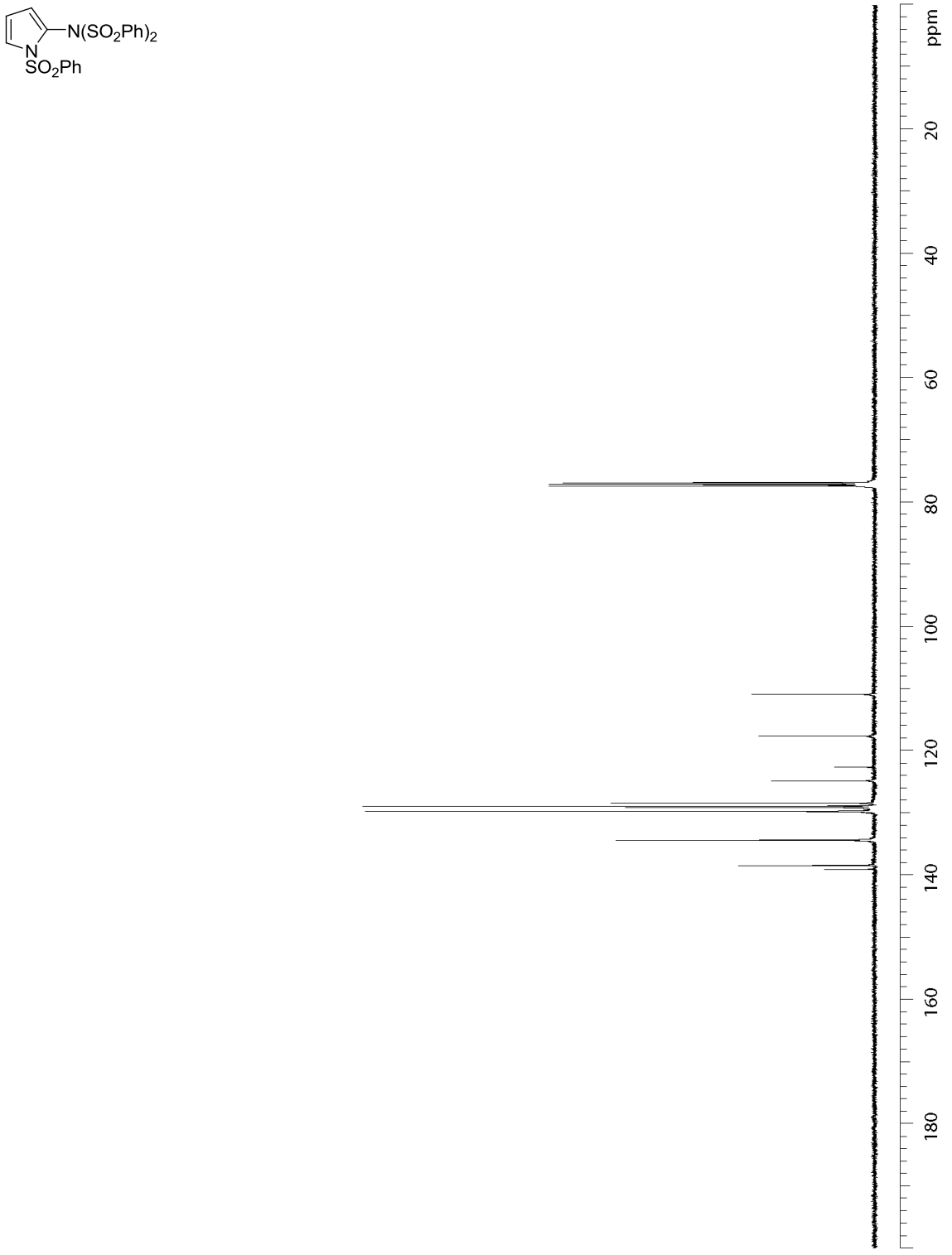
$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2u**



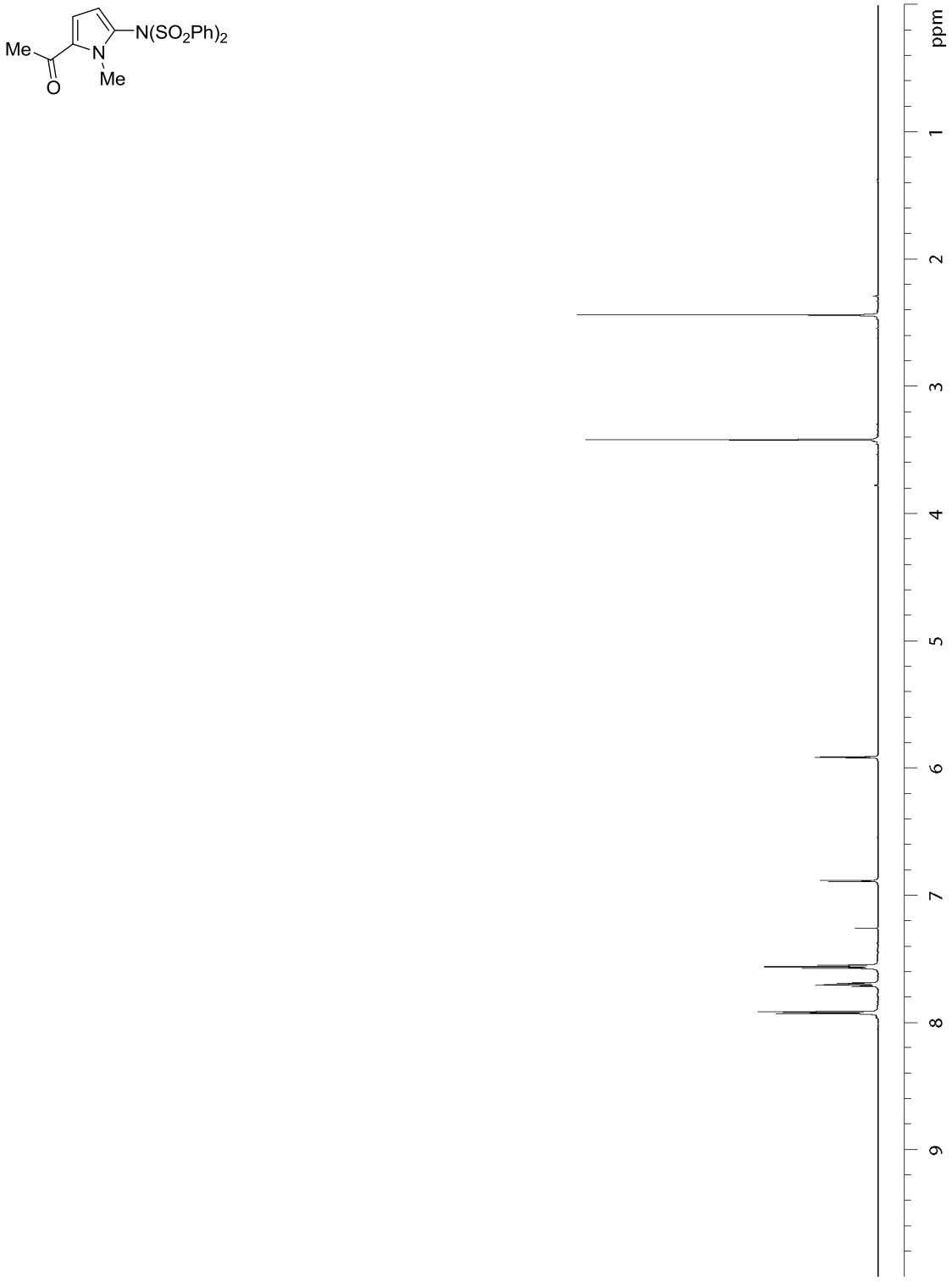
$^1$H NMR ($CDCl_3$, 23 ºC) of **2v**



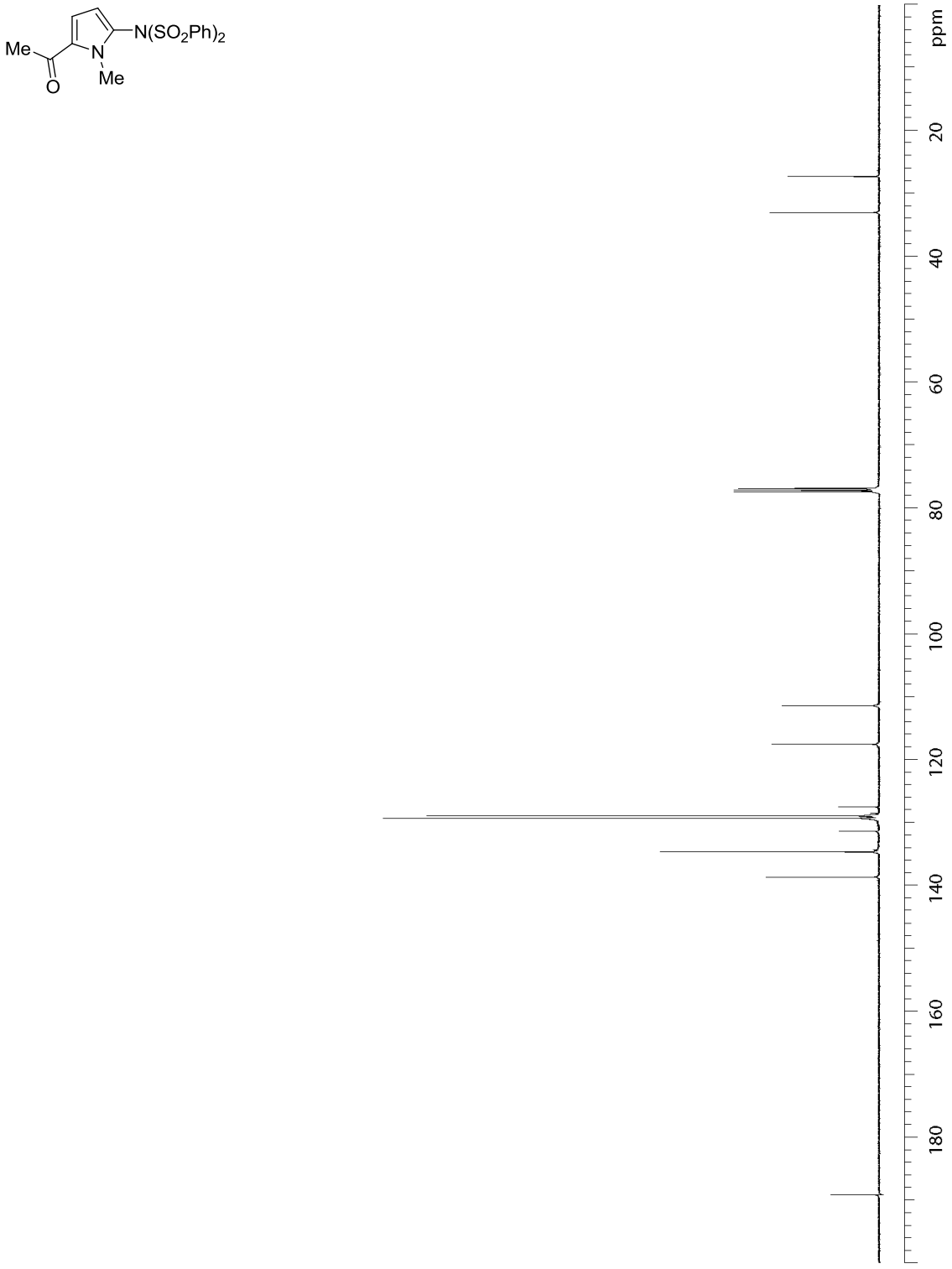
$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2v**



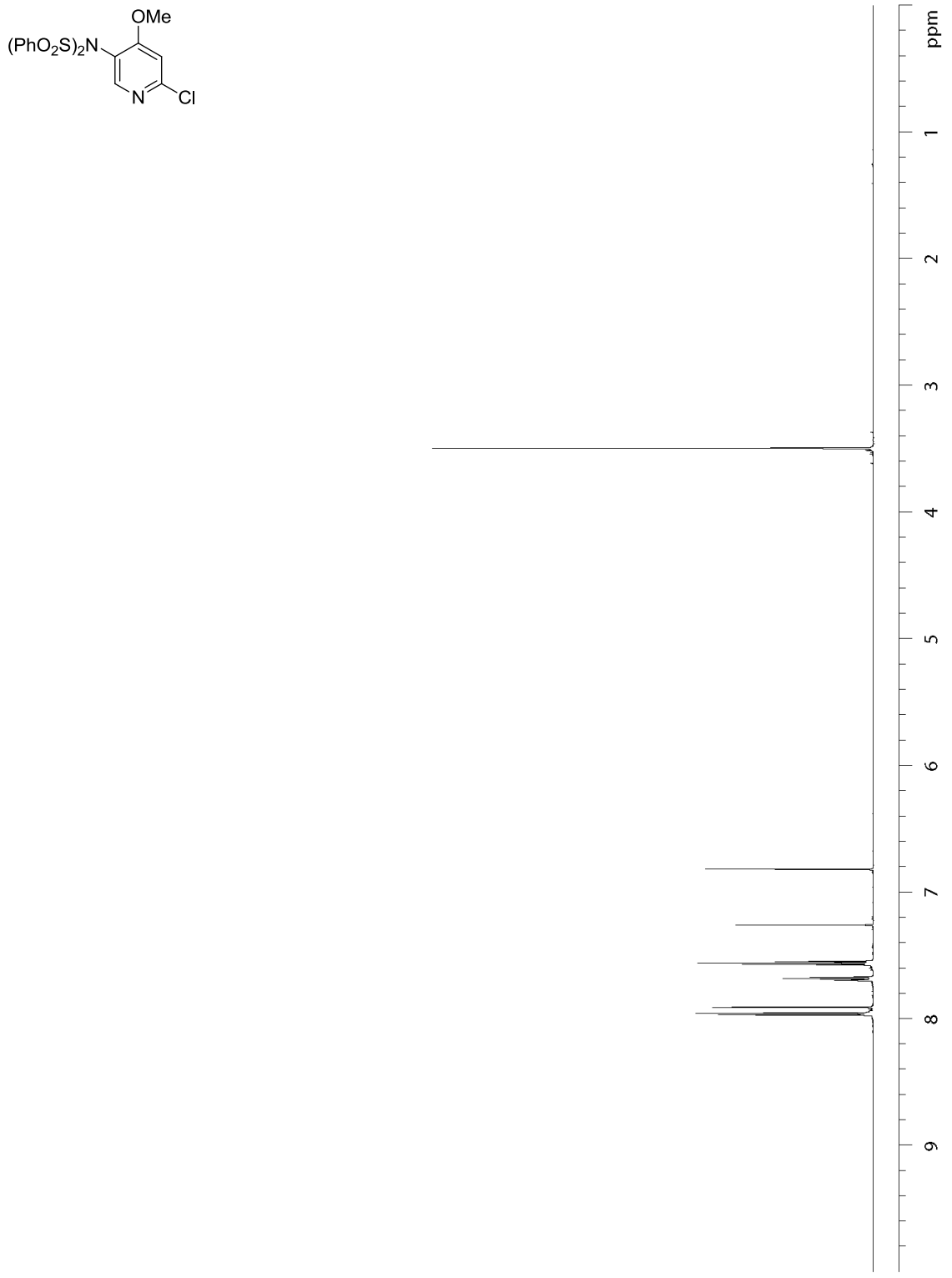
$^1$H NMR ($CDCl_3$, 23 ºC) of **2w**



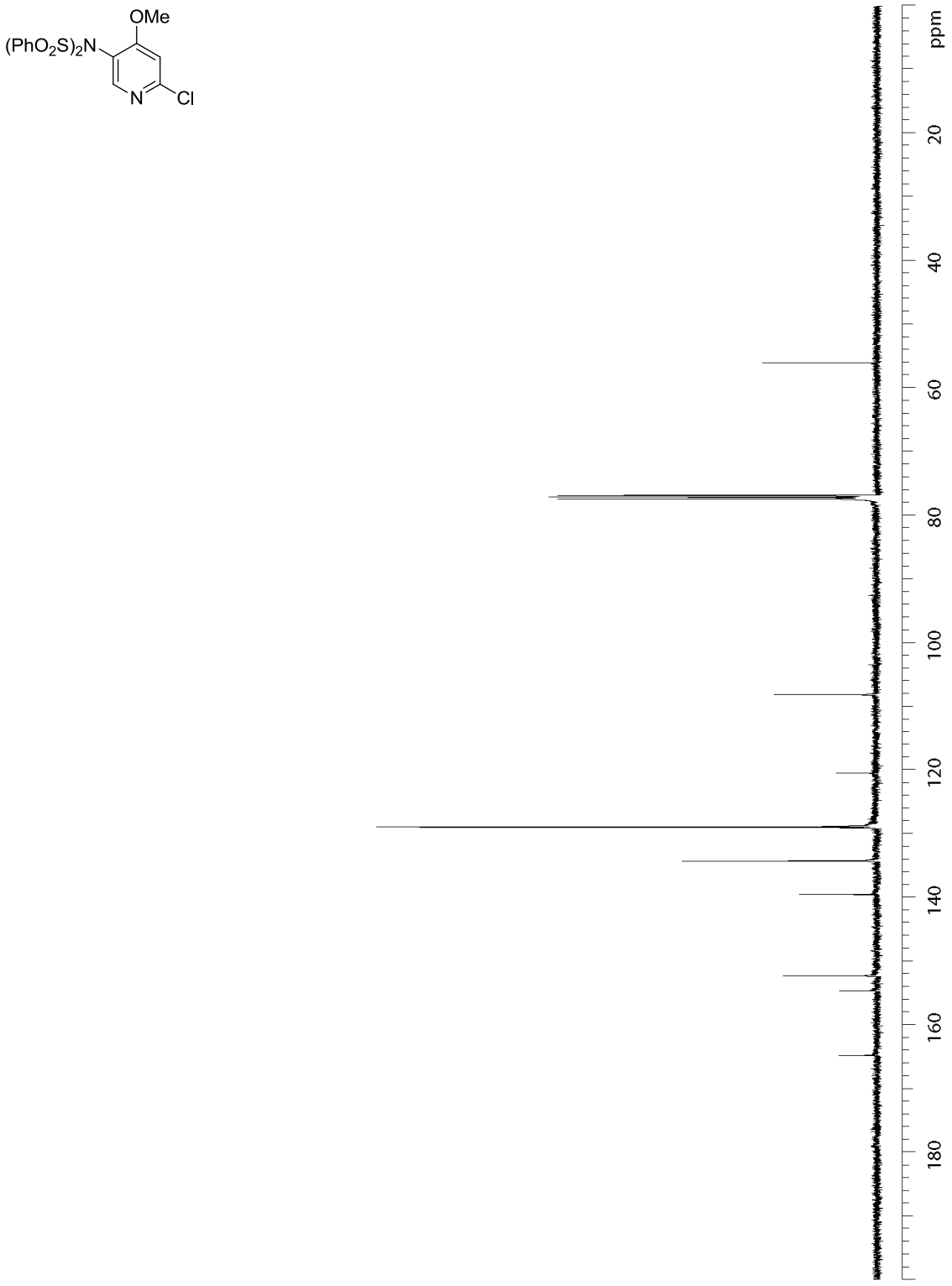
$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2w**



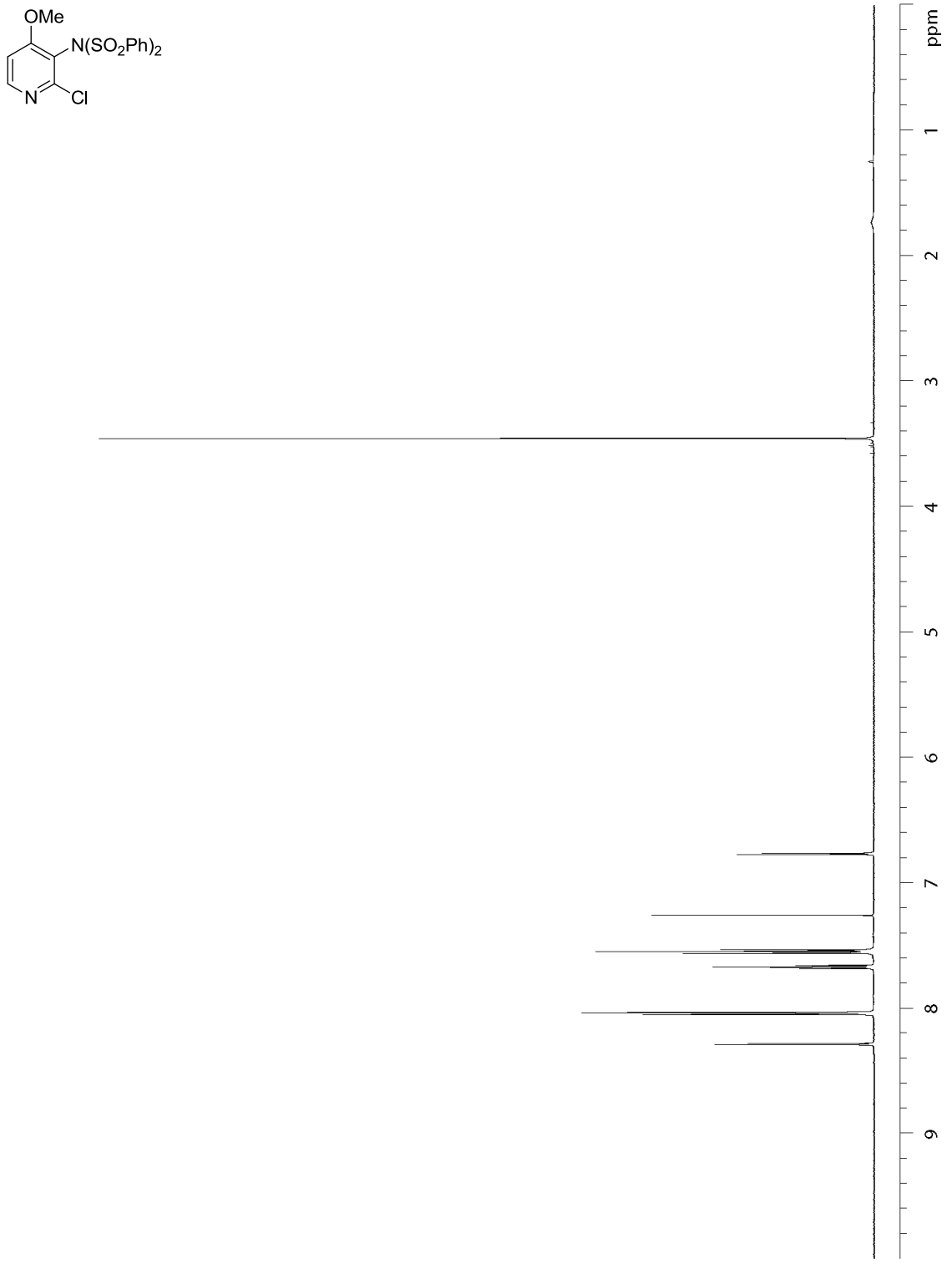
$^1$H NMR ($CDCl_3$, 23 ºC) of **2x**



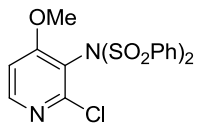
$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2x**

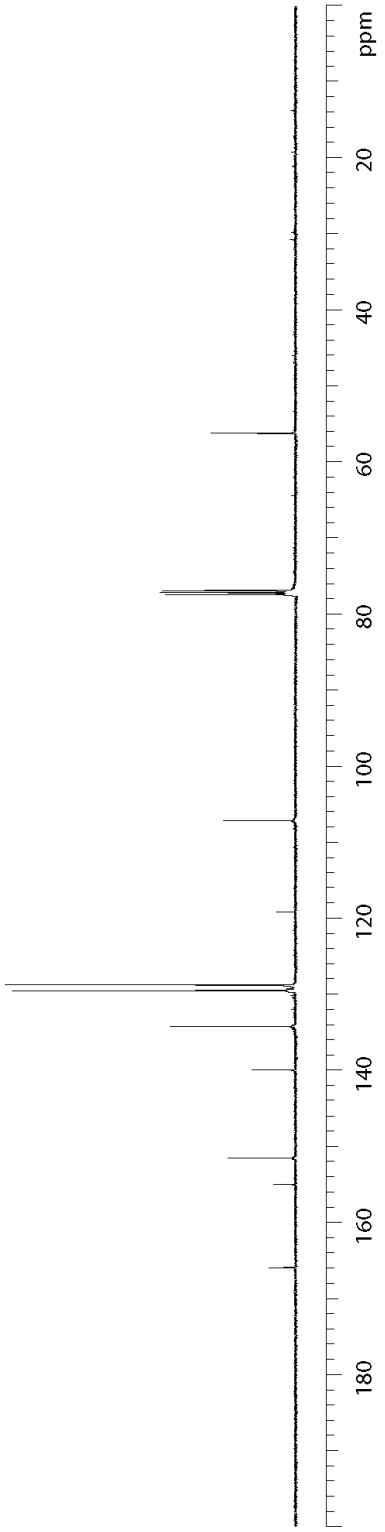


$^1$H NMR ($CDCl_3$, 23 ºC) of **2x-II**

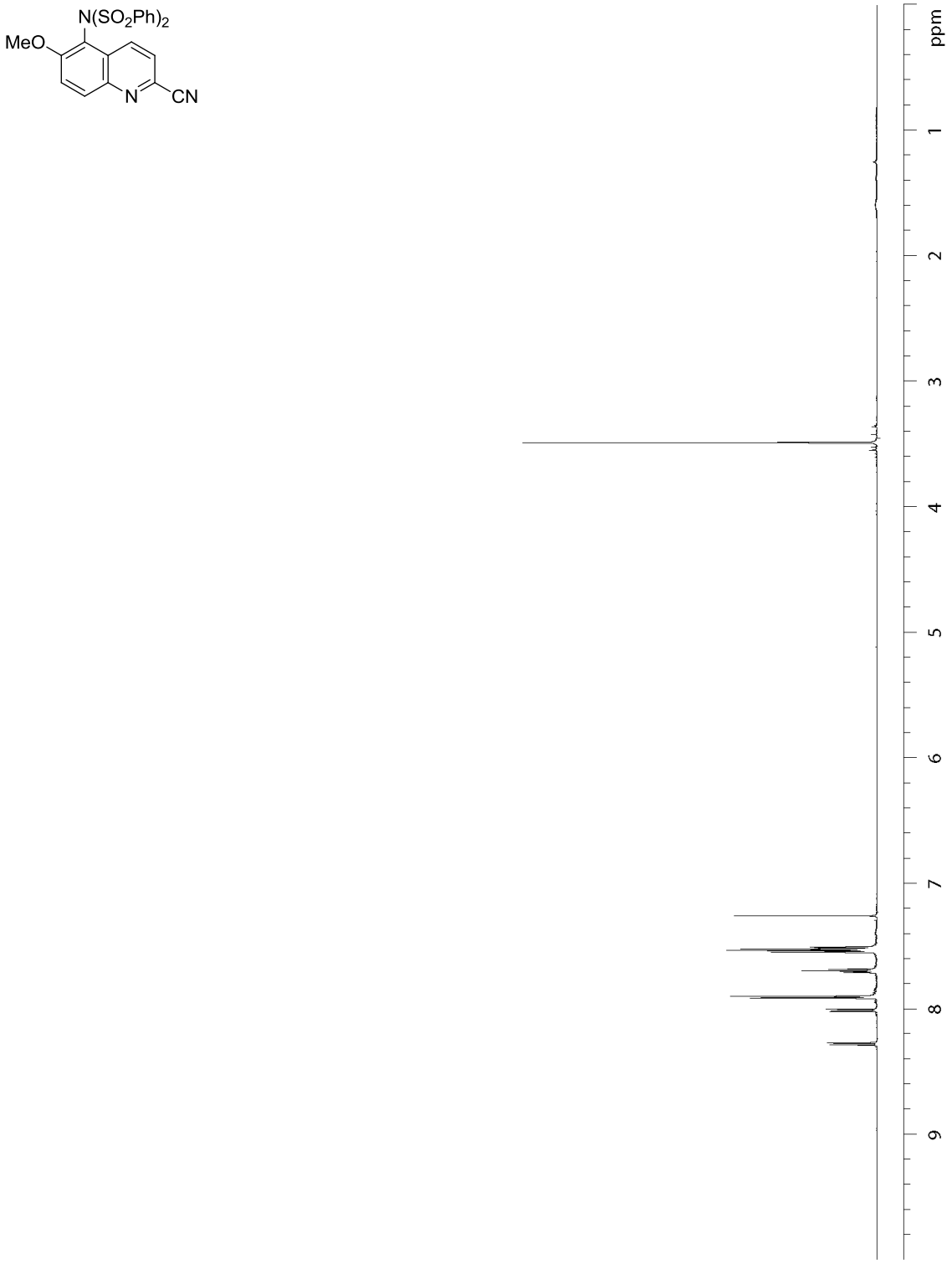


$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2x-II**

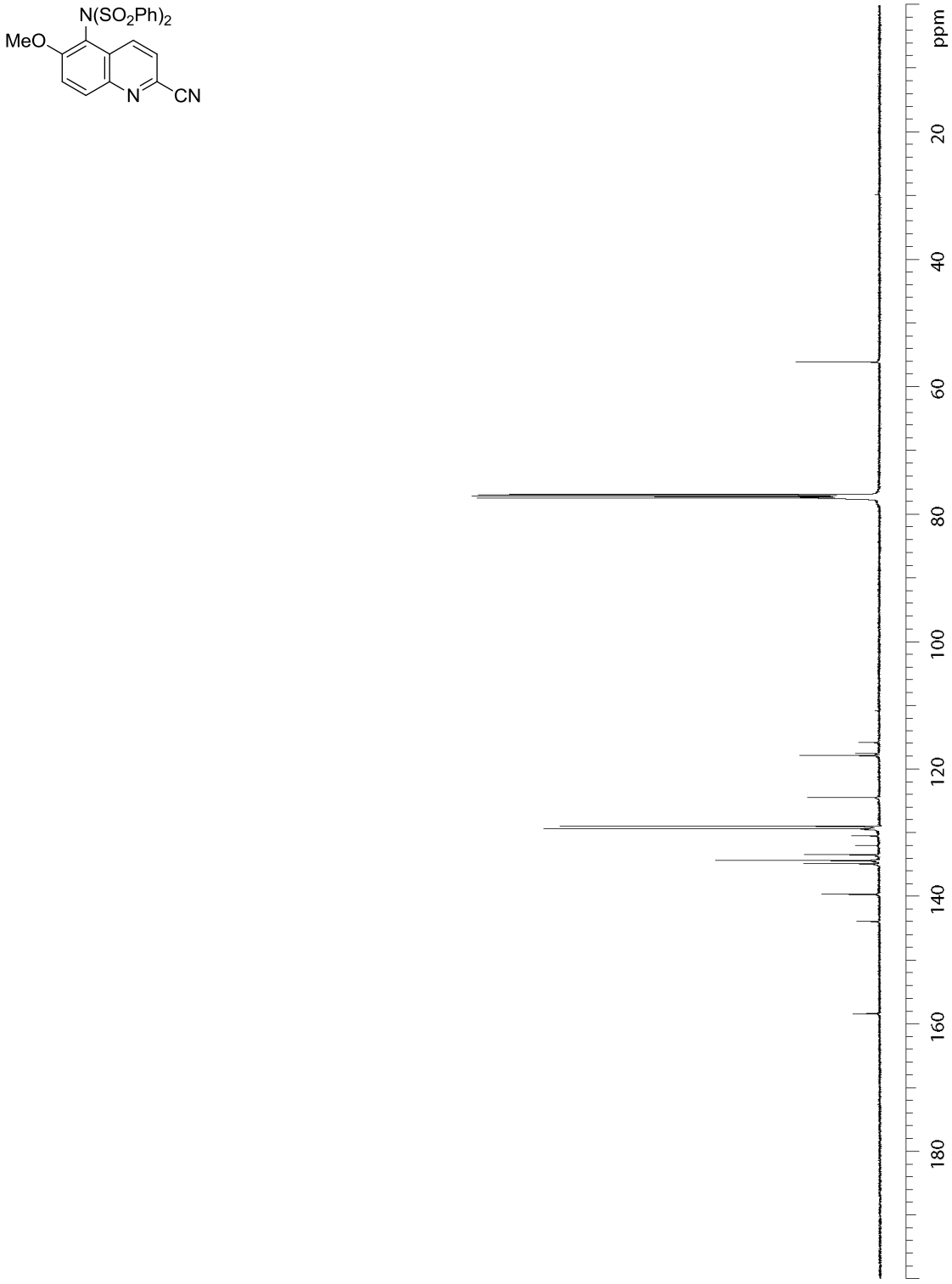


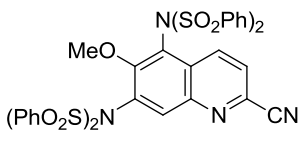
$^1$H NMR ($CDCl_3$, 23 ºC) of **2y**

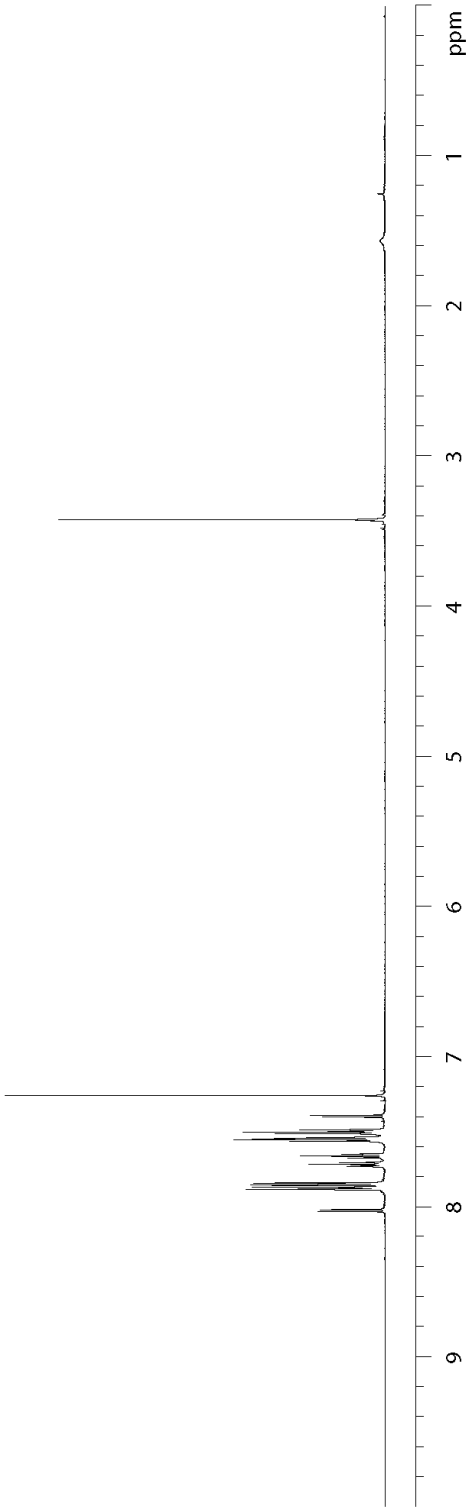


$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2y**

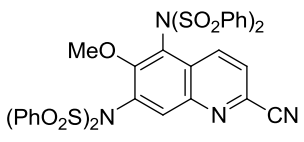


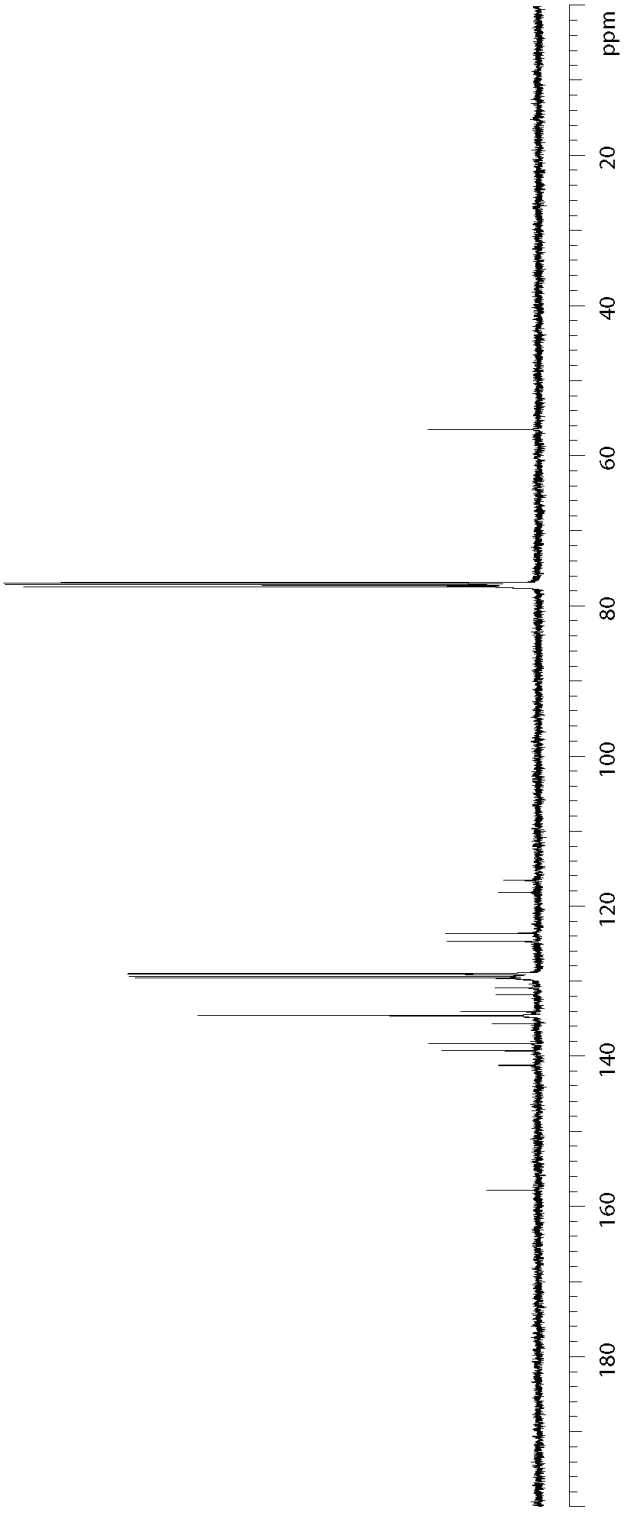
$^1$H NMR ($CDCl_3$, 23 ºC) of **2y-II**



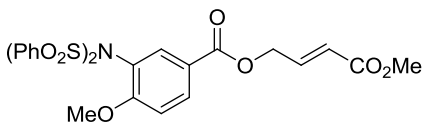



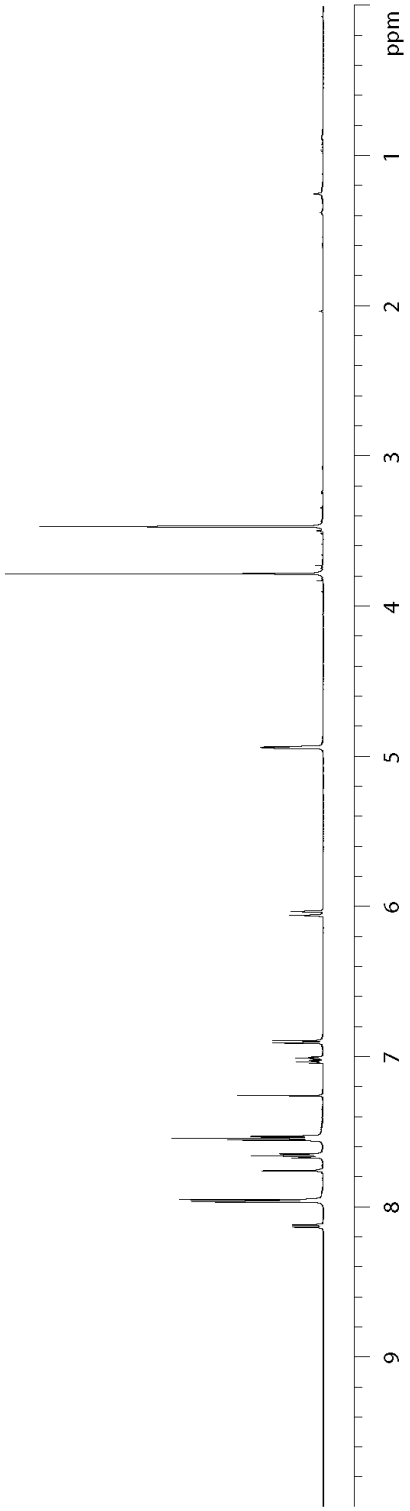
$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2y-II**



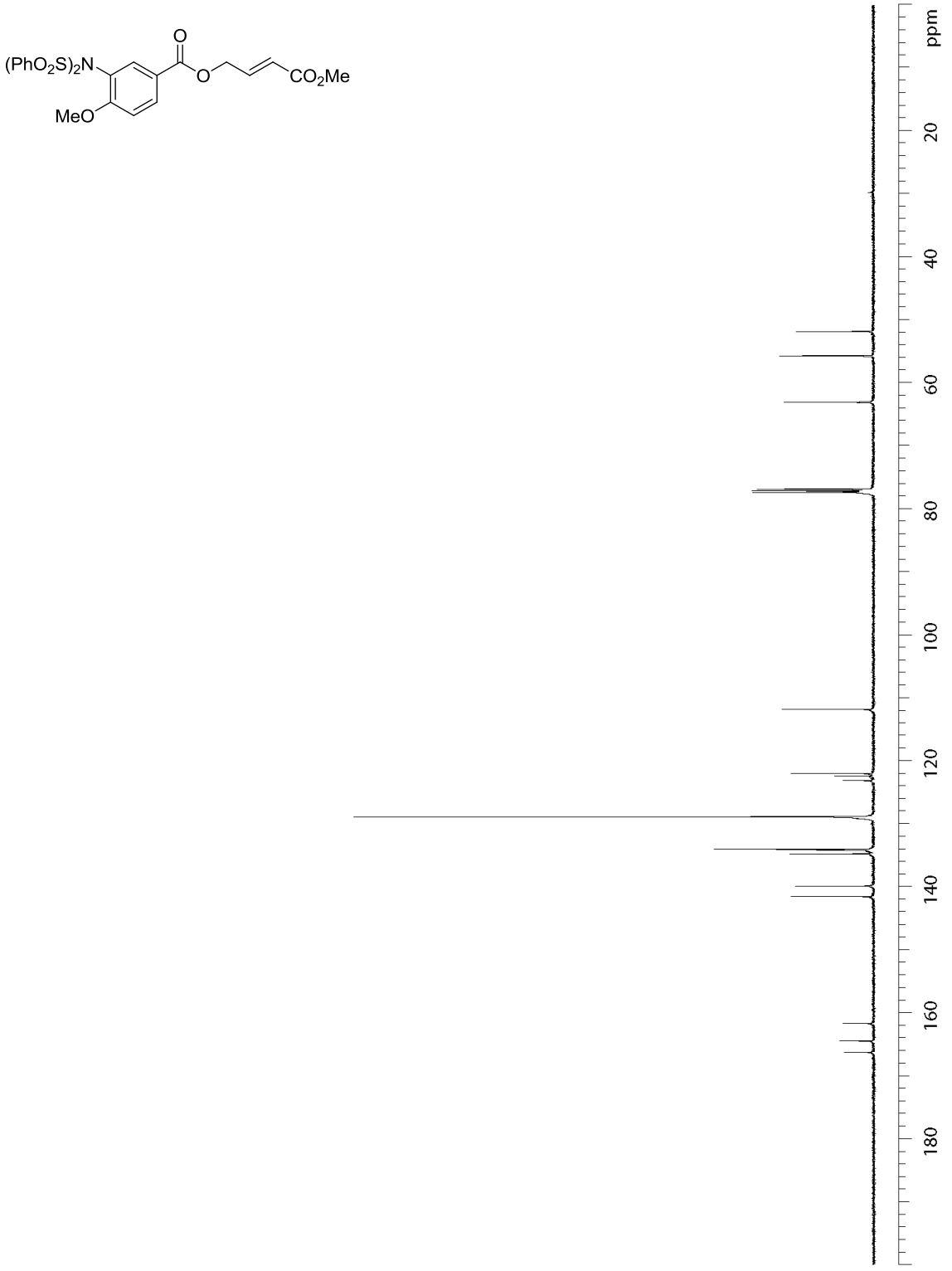



$^1$H NMR ($CDCl_3$, 23 ºC) of **2z**

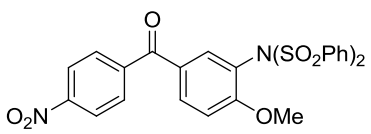


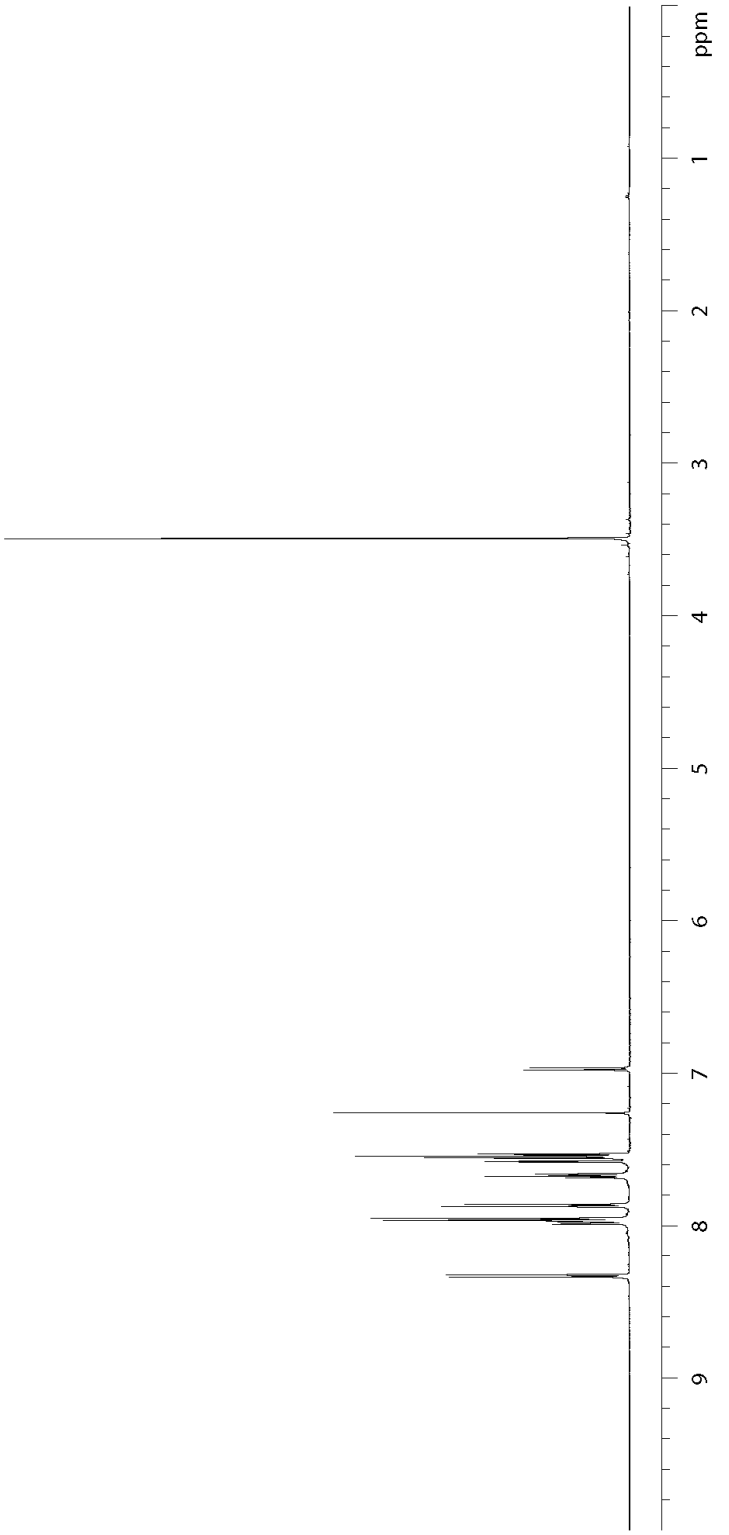



$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2z**

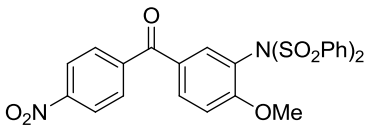


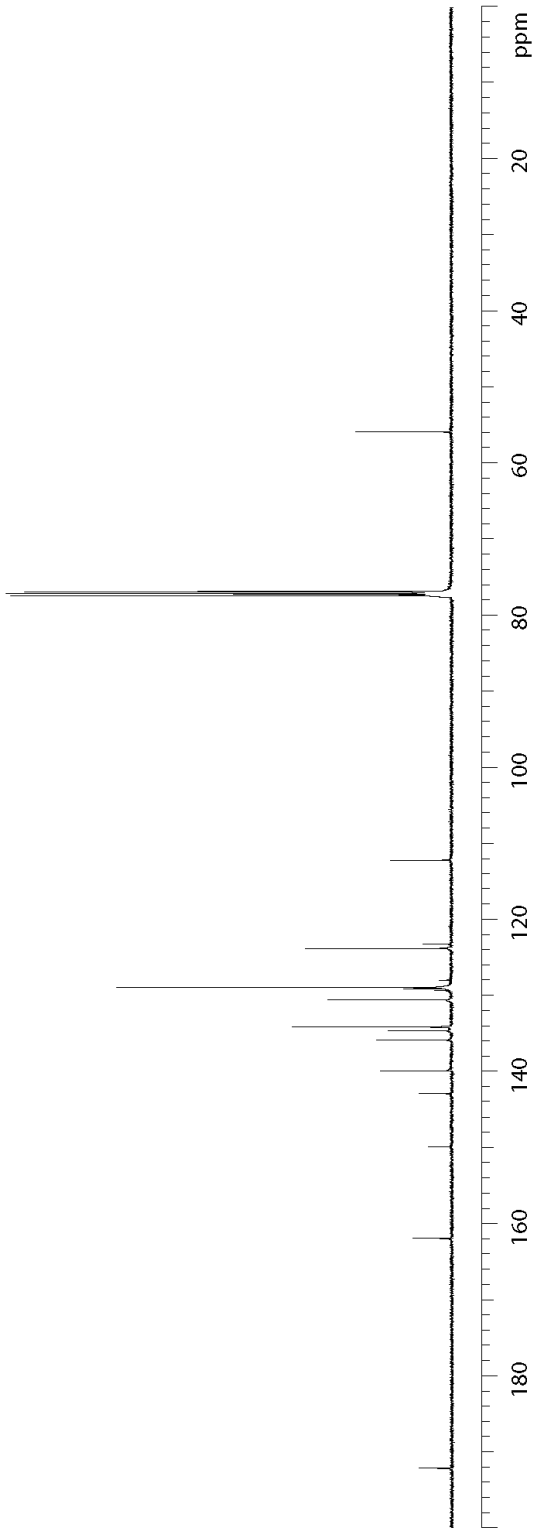
$^1$H NMR ($CDCl_3$, 23 ºC) of **2aa**



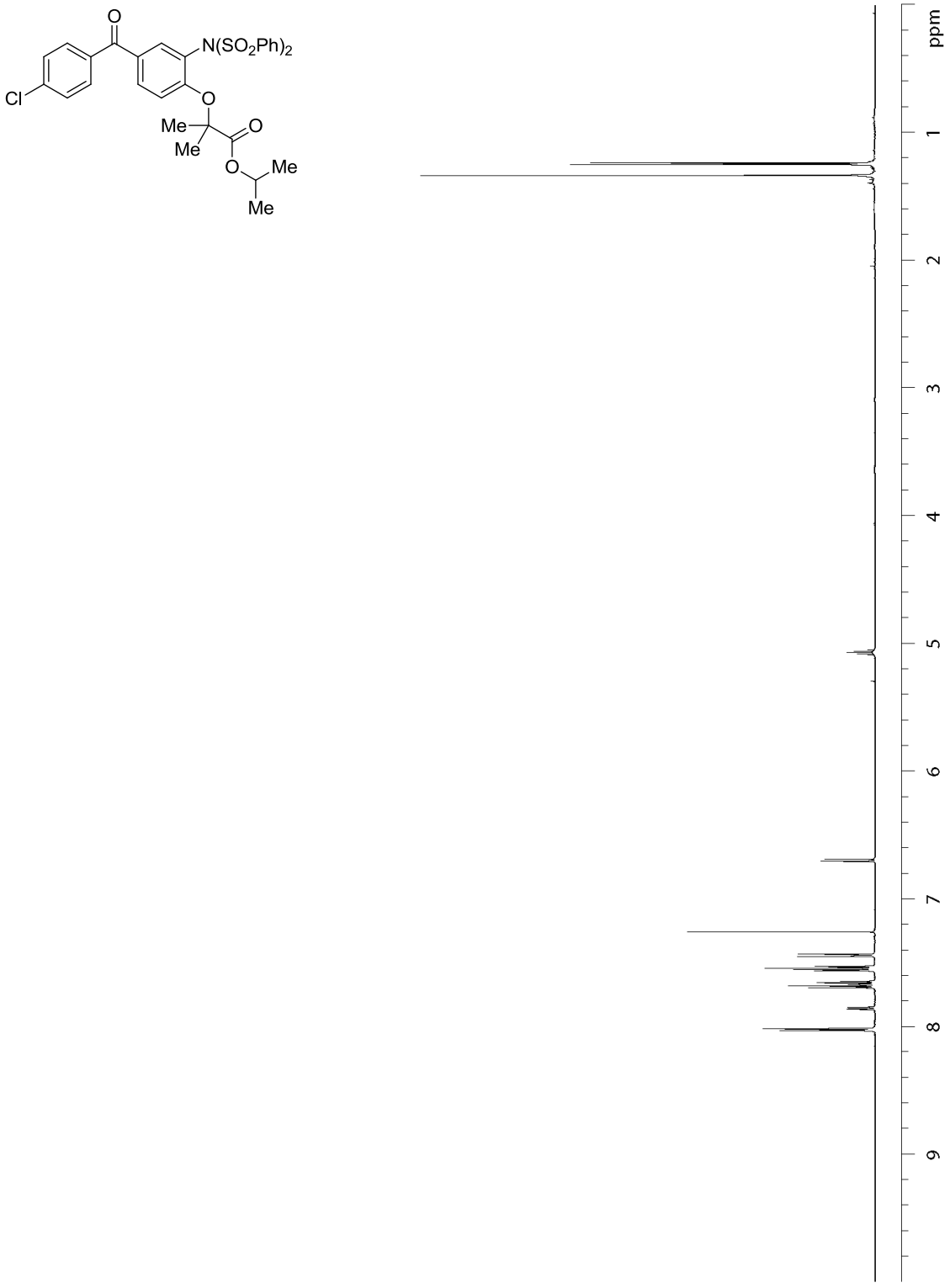



$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2aa**

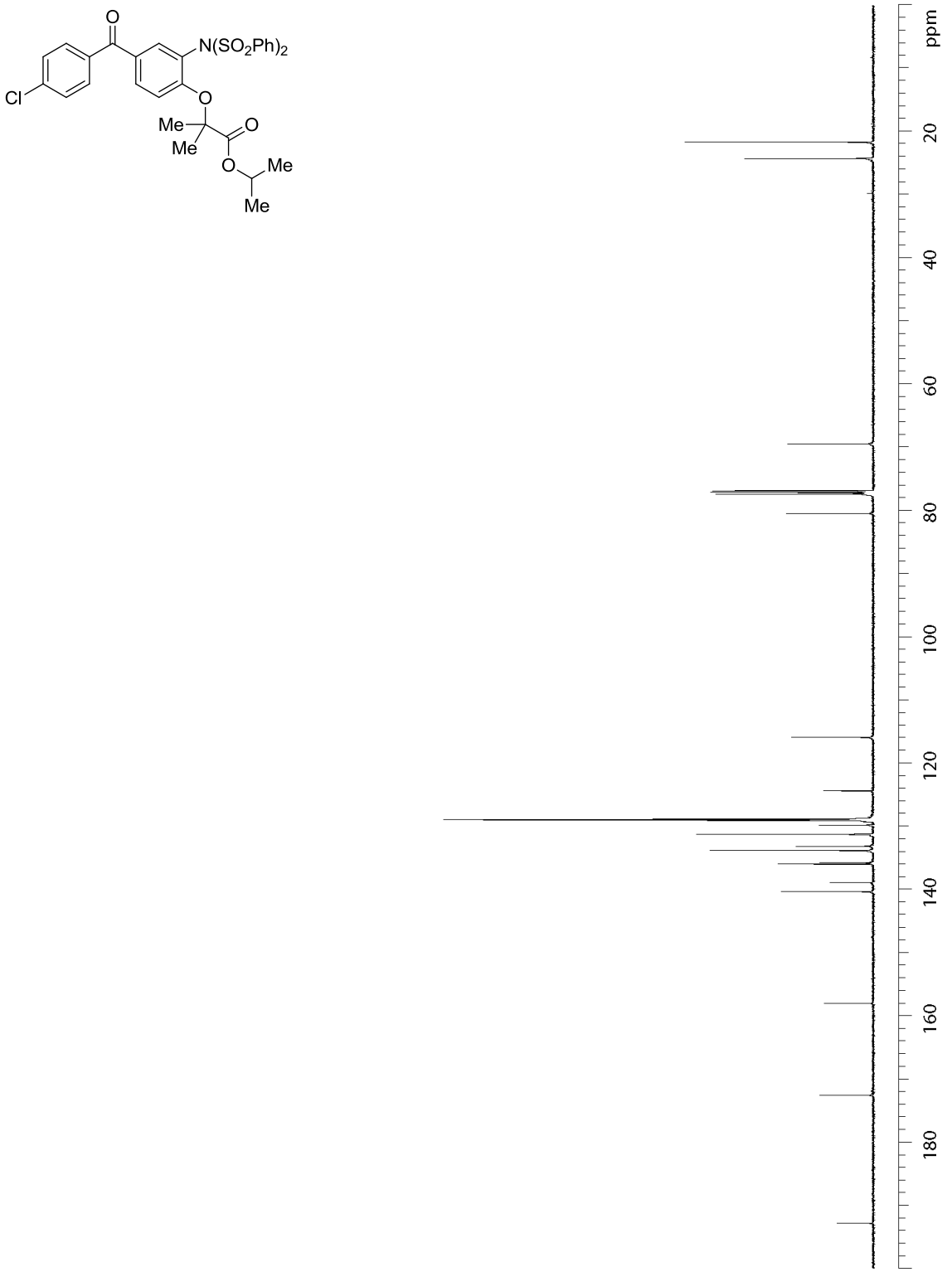


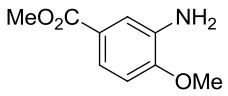
$^1$H NMR ($CDCl_3$, 23 ºC) of **2ab**

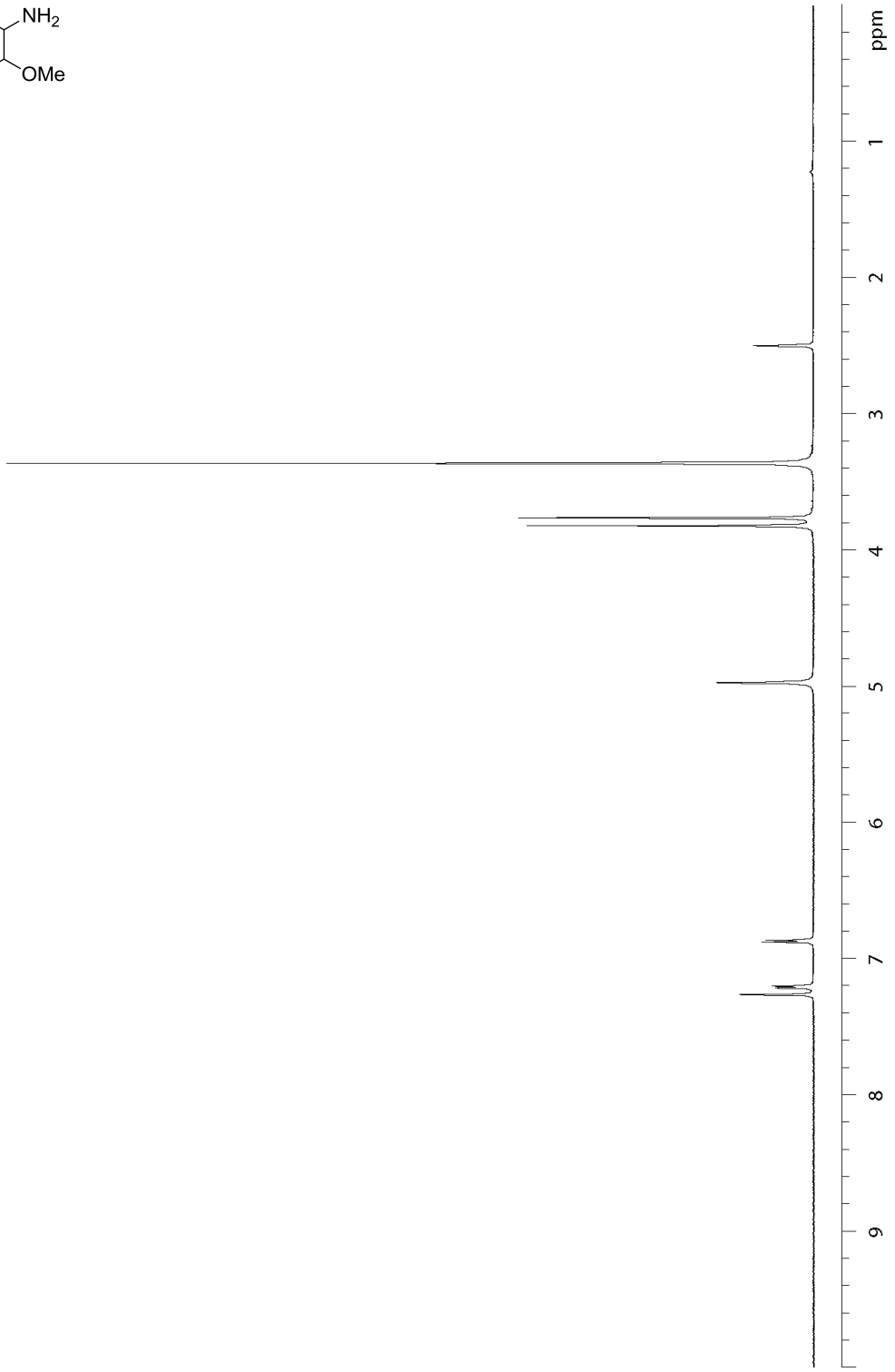


$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **2ab**



$^1$H NMR ($(CD_3)_2SO$, 23 ºC) of **3b**



$^{13}$C NMR ((CD$_3$)$_2$SO, 23 ºC) of **3b**