CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Biaryls Made Easy: *PEPPSI* and the Kumada-Tamao-Corriu Reaction

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General Experimental

All reagents were purchased from commercial sources and were used without further purification, unless otherwise stated. Dry DMI and DME (stored over 4Å molecular sieves) were purchased from Fluka and Aldrich, respectively, and handled under argon. Reagent-grade THF was dried under argon over sodium benzophenone. Anhydrous LiCl was purchased from Aldrich and handled in a glove box. Technical grade pentane, ethyl acetate and dichloromethane were used directly from the drum without further purification. All reaction vials (screw-cap threaded, caps attached, 17 x 60 mm) were purchased from Fischer Scientific. $CDCl_3$ was purchased from Cambridge Isotopes. Thin Layer Chromatography (TLC) was performed on Whattman 60 F_{254} pre-coated glass plates and spots were visualized using UV light (254 nm), potassium permanganate, or phosphomolybdic acid stains. Column chromatography purifications were carried out using the flash technique on Silicycle silica gel 60 (230-400 mesh). NMR spectra were recorded on Bruker 300 AVANCE and Bruker 400 AVANCE spectrometers. The chemical shifts (d) for ^{1}H are given in parts per million (ppm) referenced to the residual proton signal of the deuterated solvent ($CHCl_3$ at d 7.26 ppm); coupling constants are expressed in hertz (Hz). ^{13}C NMR spectra were referenced to a $CDCl_3$ signal (77.0 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, m = mulitplet, dd = doublet of doublets, q = quartet, and qn = quintet. For ^{13}C APT spectra, a positive set of peaks (indicated by +) represent quaternary carbons, as well as carbon atoms with an even number of protons; a negative set of peaks (indicated by -) represent carbon atoms with an odd number of protons. Gas chromatography was performed on a Varian

Series GC/MS/MS 4000 System and the reported yields are based over a calibrated area of undecane as the internal standard. Melting points were determined using a Fisher-Johns melting point apparatus and are uncorrected. All experiments were conducted under an atmosphere of dry argon.

Synthetic Procedures

Synthesis of p-methoxyphenylmagnesium bromide (1M solution in THF) A 50 mL round-bottom flask equipped with a stir-bar, reflux condenser, and a rubber septum was flame-dried *in vacuo* until no visible moisture was detected on the glass. The apparatus was then purged with argon and allowed to cool to room temperature; this process was repeated twice more to ensure complete dryness. A second 50 mL round-bottom flask with stir-bar was also flame-dried using the same procedure. While cooling under argon, oxide-free magnesium metal turnings (0.88g, 36 mmol) were weighed out in a vial, to which a small crystal of iodine was added. The contents of the vial were transferred to the first flask under a cone of argon, which was then re-sealed and purged with argon. Two mL of THF were added to the first flask, solvating the iodine crystal forming a brown solution. To the second round-bottomed flask was added *p*-bromoanisole (3.75 mL, 30 mmol) along with the remaining THF (26.25 mL). A few drops of this mixture were cannulated into the first flask, until the brownish colour disappeared. The reaction was then initiated by warming with a heat gun and the remaining halide was cannulated dropwise to the first flask maintaining a steady exotherm. Following cannulation, the Grignard solution was warmed to reflux under argon for 16 h. A 10 uL sample was withdrawn and quenched with 100 µL water and extracted with 2 mL of hexanes. The

organic layer was passed through a plug of silica gel and analyzed by GC-MS. One single peak corresponding to anisole was observed, ensuring Grignard formation.

Synthesis of p-tolylmagnesium bromide (1M solution in THF) The procedure for *p*-methoxyphenylmagnesium bromide was used with the following exceptions: *p*-bromotoluene (3.14 mL, 25 mmol), 720 mg Mg turnings (30 mmol) and 21.86 mL of THF were used to generate the Grignard and no initiation with I_2 was necessary. The freshly-prepared reagent was allowed to cool to RT, and was ready for use after approximately 3h.

Synthesis of o-methoxyphenylmagnesium bromide (1M solution in THF) Following the procedure for *p*-methoxyphenylmagnesium bromide and using a 100 mL round-bottom flask, *o*-bromoanisole (6.2 mL, 50 mmol) was diluted with THF (43.8 mL) and cannulated into the flask containing the Mg turnings (1.46g, 60 mmol) and iodine. The mixture was initially warmed with a heat gun, followed by stirring under argon prior to use.

Synthesis of 5-acenaphthylmagnesium bromide (1M solution in THF). Following the procedure for *p*-methoxyphenylmagnesium bromide and using a 10 mL round-bottom flask, 5-bromoacenaphthene (1.175 g, 5 mmol) was weighed out in a vial and then transferred under a cone of argon to a second, flame-dried, 10 mL round-bottom flask. Just enough THF was added to dissolve the aryl bromide and this concentrated mixture was added dropwise to the flask containing the Mg turnings (146 mg, 6 mmol) and

iodine. Grignard formation was initiated by warming with a heat gun and the bromide was added at a rate sufficient to maintain a gentle reflux. Following Grignard formation, additional THF was added to bring the final volume to 5 mL. The reagent was stirred under argon prior to use.

Synthesis of 2-thiopheneylmagnesium bromide (1M solution in THF) Following the procedure for *p*-methoxyphenylmagnesium bromide, 2-bromothiophene (1.9 mL, 20 mmol) was diluted with THF and added dropwise to the Mg-containing flask (0.5 mg, 20.6 mmol), while maintaining a steady exotherm. Initially, a few drops of the concentrated aryl bromide were used to initiate the Mg surface, and the final solution was diluted up to 20 mL. Following cannulation, the reaction was stirred under argon prior to use.

Synthesis of mesitylmagnesium bromide (1M solution in THF) Following the procedure for *p*-methoxyphenylmagnesium bromide, 2-bromomesitylene (3.86 mL, 25 mmol) was diluted with THF (21.14 mL) and added dropwise to the Mg-containing flask, while maintaining a steady exotherm. Following cannulation, the reagent was allowed to stir under argon at RT prior to use.

Synthesis of p-chlorophenylmagnesium bromide (1M solution in THF) Following the procedure for *p*-methoxyphenylmagnesium bromide (omit iodine addition) and using a 25 mL round-bottom flask, a portion of a solution of *p*-bromochlorobenzene (3.83 g, 20 mmol) dissolved in 4 mL of THF was added dropwise to the flask containing the Mg

turnings (0.528 g, 20 mmol). Upon exotherm, the Grignard was added at a rate sufficient to maintain a gentle reflux while alternating with fresh THF. Following Grignard formation, additional THF was added to bring the final volume to 20 mL. The reagent was stirred under argon at RT prior to use.

Synthesis of NHC-$PdCl_2$-3-chloropyridine complexes: In air, a vial was charged with $PdCl_2$ (177 mg, 1.0 mmol), NHC?HCl, (1.1 mmol), K_2CO_3 (691 mg, 5.0 mmol) and a stir-bar. 3-chloropyridine (4.0 mL) was added, the vial was capped with a Teflon®-lined screw cap and heated with vigorous stirring for 16h at 90°C. After cooling to RT, the reaction mixture was diluted with CH_2Cl_2 and passed through a short pad of silica gel covered with a pad of Celite eluting with CH_2Cl_2 until the product was completely recovered. Most of the CH_2Cl_2 was removed (rotary evaporator) at RT, and the 3-chloropyridine was then vacuum-distilled (water aspirator vacuum) and saved for reuse. The pure complexes **1-4** were isolating after washing with pentane, decanting of the supernatant and drying in high vacuum.

Cross-coupling procedures

Some cross-coupling reactions were run with a final solvent volume of 1.6 to 2.1 mL (0.5 mmol), while others include a final solvent volume of 0.4 mL (0.25 mmol), and 0.8 mL (0.5 mmol). A specific solvent ratio for each reaction is listed within the experimental results for each isolated compound following the general procedures.

Kumada-Tamao-Corriu aryl-aryl cross-coupling procedures.

Procedure A:

In air, a vial equipped with a stir-bar was charged with complex **1** (6.8 mg, 2 mol %), sealed with a septum, and purged with argon. Distilled THF (0.26 to 0.7 mL) and dry DMI (0.53 to 0.7 mL) were added by syringe and stirred for 1-2 minutes, after which the aryl halide (0.5 mmol), and *n*-undecane (GC/MS internal standard, 50 µL) were injected via syringe. Alternatively, if the aryl halide was solid at room temperature, it was weighed out and added to the vial in air following complex **1** addition. After 1-2 minutes of stirring, the Grignard reagent (0.65 to 0.8 mmol, 1.3 to 1.6 Eq.) was added in one rapid shot by syringe. The septum was replaced with a Teflon®-lined screw cap under an inert atmosphere and the reaction mixture was allowed to stir for approximately 24 hours at RT/50°C prior to GC/MS and/or TLC analysis. Once product was identified, the general work-up procedure for compound isolation was followed.

Procedure B:

In air, a vial equipped with a stir-bar was charged with complex **1** or **2** (6.8 mg, 2 mol %), sealed with a septum, and purged with argon. Dry THF (0.35 mL) and dry DME (0.8 to 1.0 mL) was added by syringe and stirred for 1-2 minutes, after which the aryl halide (0.5 mmol), and *n*-undecane (GC/MS internal standard, 50 µL) were injected via syringe. Alternatively, if the aryl halide was solid at room temperature, it was weighed out and added to the vial in air following complex **1** addition. After 1-2 minutes of stirring, the

Grignard reagent (1.3 to 1.6 Eq.) was added in one rapid shot by syringe. The septum was replaced with a Teflon®-lined screw cap under an inert atmosphere and the reaction mixture was allowed to stir for approximately 24 hours at RT or 50°C prior to GC/MS and/or TLC analysis. Once product was identified, the general work-up procedure for compound isolation was followed.

Procedure C:

In air, a vial equipped with a stir-bar was charged with complex **1** or **2** (6.8 mg, 2 mol %), sealed with a septum, and purged with argon. The aryl halide (0.5 mmol), and *n*-undecane (only for GC/MS analysis, internal standard, 50 µL) were injected via syringe. Alternatively, if the aryl halide was solid at room temperature, it was weighed out and added to the vial in air following complex **1** (or **2**) addition. The Grignard reagent (0.8 mmol, 1.6 Eq.) was added in one rapid shot by syringe, followed by septum replacement for a Teflon®-lined screw cap under an inert atmosphere. The reaction mixture was allowed to stir for approximately 24 hours at RT/60°C prior to GC/MS and/or TLC analysis. Once product was identified, the general work-up procedure for compound isolation was followed.

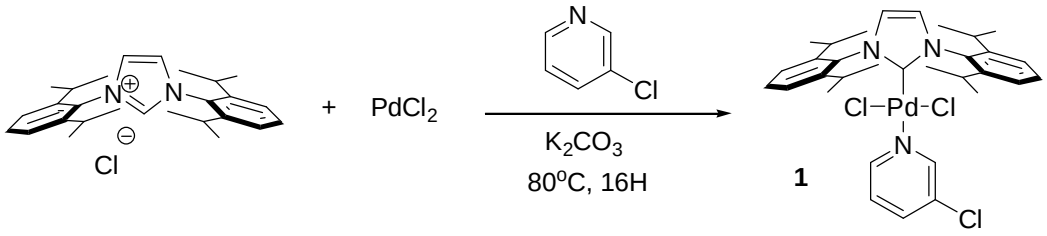
Sequential cross-coupling (SCR) procedure:

In air, a 10mL round bottom flask equipped with a stir-bar was charged with complex **1** (6.8 mg, 2 mol %), sealed with a septum, and purged with argon (3). To this was added directly the aryl halide (0.5 mmol) followed by the first Grignard reagent (0.6 mmol, 1.2 Eq). The resulting mixture was allowed to stir at room temperature for the specified

amount of time. When the reaction was deemed complete by TLC analysis, the second Grignard reagent (0.8 mmol, 1.6 Eq) was added. The resulting solution was allowed to stir at the specified temperature for the specified period of time. Once product was identified, the general work-up procedure for compound isolation was followed.

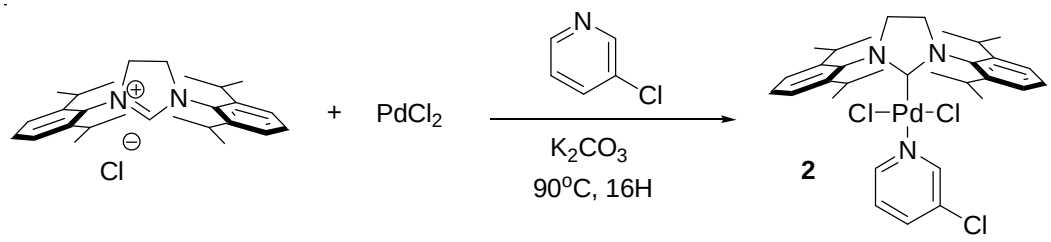
Experimental Work-Up for Product Isolation.

When couplings were judged complete, a 1M Na_3EDTA solution (prepared from EDTA and 3 eq. NaOH) was added, the solution stirred for a minute and then transferred to a separatory funnel. The layers were separated and the aqueous layer extracted with diethyl ether (20 mL). The combined organic layers were then sequentially washed with distilled water and brine. After drying over anhydrous $MgSO_4$, the solution was filtered, concentrated, and the residue was purified by flash chromatography on silica gel.



PEPPSI-IPr **(1)** (677 mg, 97%) was prepared from the corresponding imidazolium salt, $PdCl_2$, 3-chloropyridine, and K_2CO_3, and was isolated as a yellow solid. M.p. = 240°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$) d: 8.62 (d, *J* = 1.6 Hz, 1H), 8.54 (d, *J* = 5.6 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 4H), 7.16 (s, 2H), 7.08 (dd, *J* = 8.0 Hz, *J* = 5.7 Hz, 1H), 3.19 (qn, *J* = 6.7 Hz, 4H), 1.52 (d, *J* = 6.8 Hz,

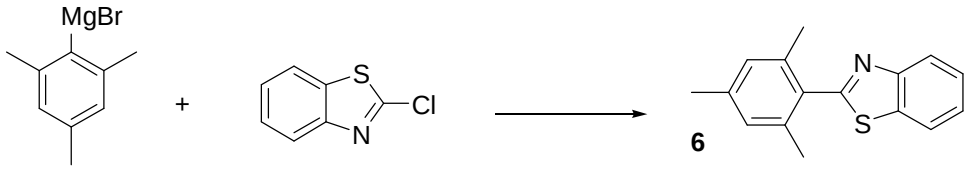
12H), 1.47 (d, *J* = 6.7 Hz, 12H); ^{13}C NMR (100.6 MHz, $CDCl_3$) d: 153.5, 150.5, 149.4, 146.7, 137.4, 135.0, 132.0, 130.3, 125.1, 124.3, 124.1, 28.7, 26.3, 23.2; Anal. Calcd. For $C_{32}H_{41}Cl_3N_3Pd$: C, 56.48; H, 6.07; N, 6.18. Found: C, 56.90; H, 5.99; N, 6.52.



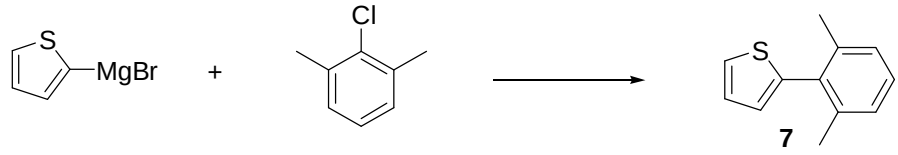
PEPPSI-SIPr **(2)** (661 mg, 88%) was prepared from the corresponding imidazolium salt, $PdCl_2$, 3-chloropyridine, and K_2CO_3, and was isolated as a yellow solid. M.p. = 198-201°C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$) d: 8.58 (s, 1H), 8.50 (d, *J* = 5.6 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 4H), 7.07 (t, *J* = 6.8 Hz, 1H), 4.09 (s, 4H), 3.60 (qn, *J* = 6.7 Hz, 4H), 1.57 (d, *J* = 4.4 Hz, 12H), 1.28 (d, *J* = 6.7 Hz, 12H); ^{13}C NMR (100.6 MHz, $CDCl_3$) d: 150.3, 149.3, 147.5, 137.4, 135.3, 131.9, 129.5, 124.4, 53.9, 28.8, 26.9, 24.2; Anal. Calcd. For $C_{32}H_{43}Cl_3N_3Pd$: C, 56.32; H, 6.35; N, 6.16. Found: C, 56.10; H, 6.07; N, 6.46.

Following *Procedure A* at 50°C using complex **1**, 1-mesityl-2-methoxybenzene **(5)** (70 mg, 62%) was prepared from 0.65 mmol of Grignard reagent and 0.5 mmol of aryl bromide, and was isolated as a crystalline, colorless solid. M.p. = 54-56°C; Lit. m.p. =

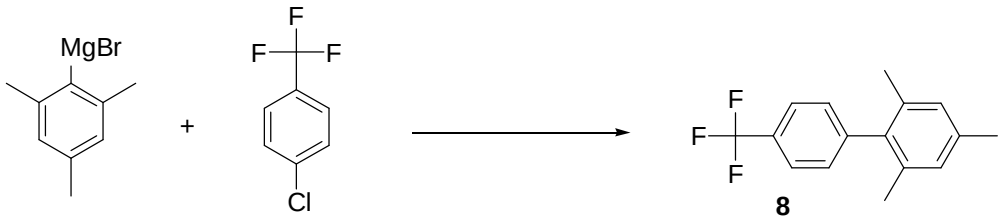
59°C;[12] R_f = 0.35 (diethyl ether/pentane, 2:98). Spectral data was in agreement with literature.[12]



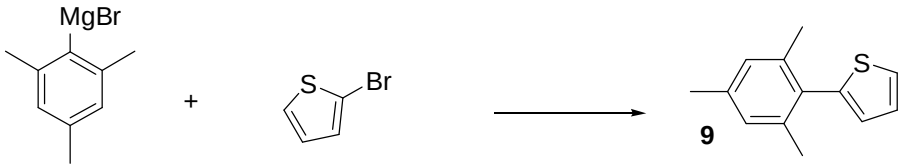
Following *Procedure C* using complex **1** at RT, 2-mesitylbenzothiazole **(6)** (115 mg, 91%) was prepared from 0.8 mmol of Grignard reagent and 0.5 mmol of aryl chloride, and was isolated as a clear, yellow oil; R_f = 0.3 (diethyl ether/pentane, 5:95); ^{1}H NMR (300 MHz, $CDCl_3$) d: 8.15 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 7.9, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H) 6.99 (s, 2H), 2.37 (s, 3H), 2.22 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) d: 167.7, 153.5, 139.4, 137.1, 129.0, 128.3, 125.9, 125.0, 123.4, 121.5, 21.2, 20.2, 15.8; Anal. Calcd. for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.53; S, 12.66. Found: C, 75.41; H, 6.25; N, 5.78; S, 12.56.



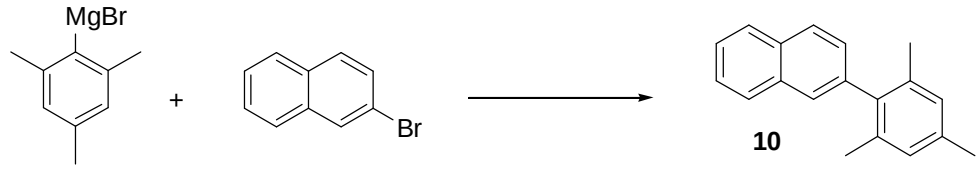
Following *Procedure B* using complex **2** at RT, 2-(2,6-dimethylphenyl)thiophene (**7**) (81.5 mg, 87%) was prepared from 0.65 mmol Grignard and 0.5 mmol of aryl chloride with LiCl additive (42 mg, 3.9 Eq.), and isolated as a viscous, clear oil; R_f = 0.5 (pentane). Spectral data was in agreement with the literature.[2]



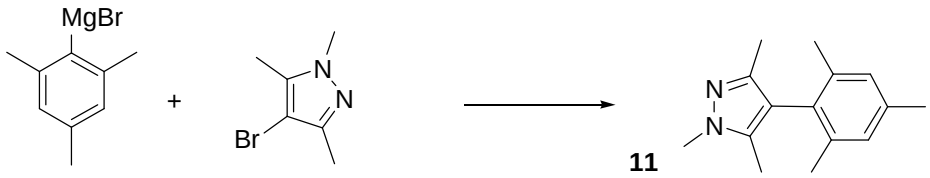
Following *Procedure C* using complex **1** at RT, 1-mesityl-4-(trifluoromethyl)benzene **(8)** (105 mg, 80%) was prepared from 0.65 mmol of Grignard reagent and 0.5 mmol of aryl chloride, and was isolated as a clear, crystalline solid. M.p. = 59-60^{o}C; Lit. m.p. = 58-59^{o}C;[10] R_f = 0.65 (pentane). ^{1}H NMR (300 MHz, $CDCl_3$) d 7.72 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.01 (s, 2H), 2.34 (s, 3H), 2.03 (s, 6H). Spectral data was in agreement with literature.[10]



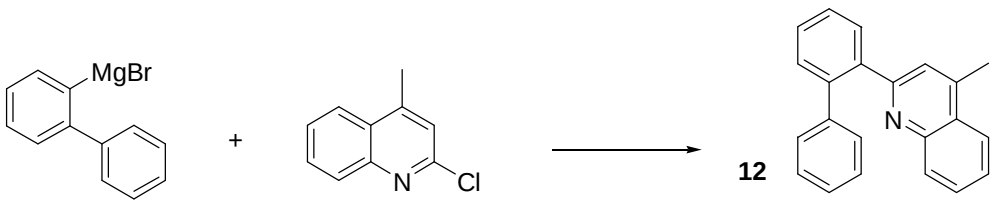
Following *Procedure C* at 50^{o}C using complex **1**, 2-mesitylthiophene **(9)** (88mg, 87%) was prepared from 0.8 mmol of Grignard reagent and 0.5 mmol of aryl bromide, and isolated as a colorless oil; R_f = 0.4 (pentane); ^{1}H NMR (300 MHz, $CDCl_3$) d: 7.42 (d, *J* = 5.2 Hz, 1H), 7.16 (t, *J* = 4.3 Hz, 1H), 7.01 (s, 2H), 6.88 (s, 1H) 2.39 (s, 3H), 2.19 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) d: 141.5, 138.3, 137.8, 131.1, 128.1, 127.0, 126.4, 125.2, 21.1, 20.7; Anal. Calcd. for $C_{13}H_{14}S$: C, 77.18; H, 6.97; S, 15.85. Found: C, 76.83; H, 7.22; S, 15.95.



Following *Procedure C* at 50°C using complex **1**, 2-mesitylnaphthalene **(10)** (113 mg, 92%) was prepared from 0.8 mmol of Grignard reagent and 0.5 mmol of aryl bromide, and was isolated as a viscous oil; R_f = 0.35 (pentane). Spectral data was in agreement with literature.[11]

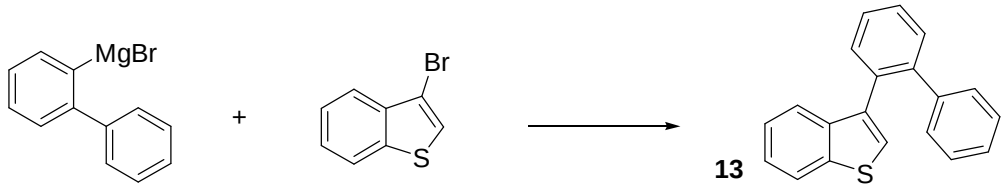


Following *Procedure C*, using complex **2** at RT, 4-mesityl-1,3,5-trimethyl-1*H*-pyrazole **(11)** (98 mg, 85%) was prepared from 0.8 mmol of Grignard reagent with 1.6 mmol of LiCl additive, 0.5 mmol of aryl bromide, and was isolated as a yellow oil; R_f = 0.2 (diethyl ether/pentane, 50:50); ^{1}H NMR (300 MHz, $CDCl_3$) d: 6.94 (s, 2H), 3.80 (s, 3H), 2.33 (s, 3H), 2.03 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) d: 145.3, 138.1, 136.6, 136.1, 129.7, 127.9, 117.0, 36.0, 21.1, 20.4, 12.1, 9.81; Anal. Calcd. for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83; N, 12.27. Found: C, 79.02; H, 8.81; N, 12.57.

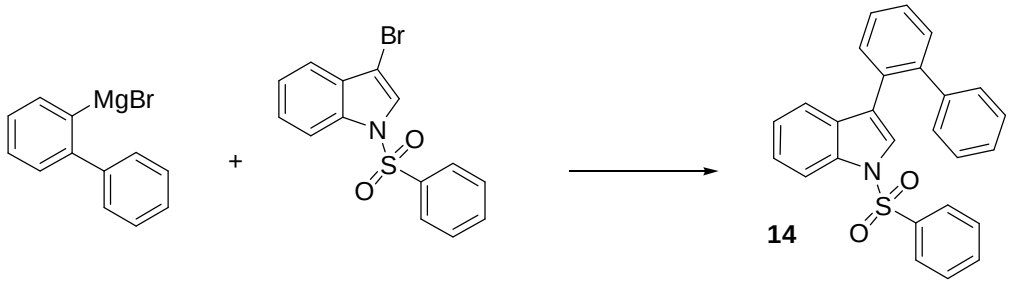


Following *Procedure C* using complex **1** at RT, 2-phenyl-(2'-phenyl)-4-methylquinoline **(12)** (69 mg, 93%) was prepared from 0.4 mmol of Grignard reagent and 0.25 mmol of

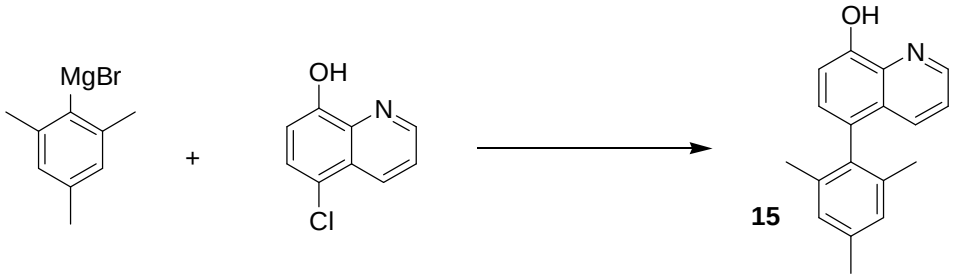
aryl chloride, and isolated as a white solid. M.p. = 116-119°C; R_f = 0.2 (diethyl ether/pentane, 10:90); ^{1}H NMR (300 MHz, $CDCl_3$) d: 8.18 (d, *J* = 8.5 Hz, 2H), 7.93(d, *J* = 8.3 Hz, 1H), 7.86 (m, 1H), 7.73 (t, *J* = 6.9 Hz, 1H), 7.58-7.51 (m, 4H), 7.23 (s, 4H), 6.82 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) d: 159.5, 148.0, 142.8, 141.2, 140.8, 139.8, 130.7, 130.4, 130.1, 129.7, 128.9, 128.7, 128.0, 127.8, 126.7, 126.6, 126.0, 124.2, 123.6, 18.4; Anal. Calcd. for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74. Found: C, 90.01; H, 5.96; N, 4.81.



Following *Procedure C*, using complex **1** at RT, 3-biphenylylbenzothiazole **(13)** (70 mg, 98%) was prepared from 0.4 mmol of Grignard reagent and 0.25 mmol of aryl bromide, and was isolated as a white solid. M.p. = 103-105°C; R_f = 0.4 (pentane); ^{1}H NMR (300 MHz, $CDCl_3$) d: 7.84 (d, *J* = 6.9 Hz, 1H), 7.57-7.47 (m, 5H), 7.29 (q, *J* = 7.2 Hz, 2H), 7.18-7.13 (m, 5H), 7.01 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d: 141.9, 141.3, 139.8, 138.7, 136.9, 134.1, 131.0, 130.5, 129.2, 129.1, 128.0, 127.8, 127.3, 126.6, 125.0, 124.0, 123.0, 122.5; Anal. Calcd. for $C_{20}H_{14}S$: C, 83.88; H, 4.93. Found: C, 83.34; H, 4.75.

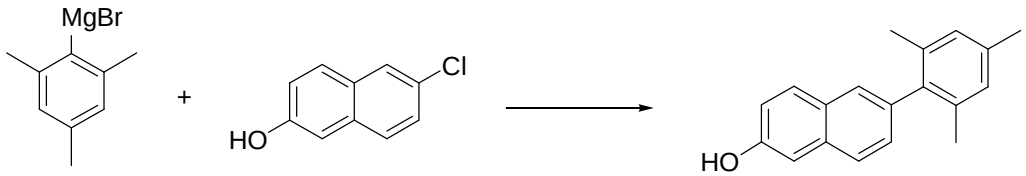


Following *Procedure C*, using complex **1** at RT, 3-biphenylyl-1-phenylsulfonyl-1*H*-indole **(14)** (79 mg, 77%) was prepared from 0.4 mmol of Grignard reagent and 0.25 mmol of aryl bromide, and isolated as a colorless, crystalline solid. M.p. = 141-144^{o}C; R_f = 0.3 (diethyl ether/pentane, 7:93); ^{1}H NMR (300 MHz, $CDCl_3$) d: 7.98 (d, *J* = 8.4 Hz, 1H), 7.71(d, *J* = 7.8 Hz, 2H), 7.60-7.52 (m, 2H), 7.48-7.42 (m, 5H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.18-7.07 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) d: 141.6, 141.3, 138.2, 134.8, 133.6, 130.8, 130.6, 130.3, 130.2, 129.2, 127.9, 127.4, 126.8, 126.6, 124.9, 124.6, 123.3, 123.2, 120.5, 113.5; Anal. Calcd. for $C_{26}H_{19}NO_2S$: C, 76.26; H, 4.68; N, 3.42. Found: C, 76.43; H, 4.61; N, 3.51.



In a glove-box, a vial equipped with a stir-bar was charged with NaH (25.2 mg, 1.05 mmol). The vial was sealed with a septum and removed from the glove-box. To the vial was added THF (0.5 mL). A solution of the aryl alcohol (180 mg, 1 mmol) dissolved in THF (0.5 mL) was added dropwise. When effervescence ceased, a solution of complex **1** (13.6 mg, 2 mol %) dissolved in THF (0.2 mL) was added via syringe, followed by the

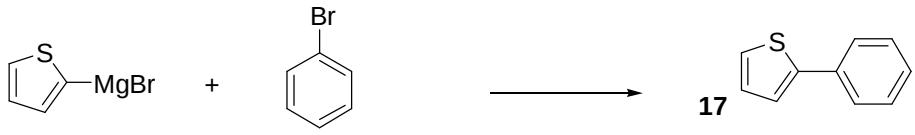
Grignard reagent (1.3 mmol, 1.3 Eq). The resulting mixture was allowed to stir for 16h at 70^{o}C furnishing 5-mesitylquinolin-8-ol **(15)** (171 mg, 65%), isolated as a yellow, crystalline solid. M.p.= 128-132^{o}C; R_f = 0.20 (dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$) d: 8.80 (s, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.34 (q, *J* = 4.3 Hz, 1H), 7.27 (s, 2H), 7.02 (s, 2H), 2.40 (s, 3H), 1.86 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) d: 151.1, 147.6, 137.4, 137.1, 134.2, 129.1, 128.2, 128.1, 121.8, 109.7, 21.1, 20.3; Anal. Calcd. for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.02; H, 6.76; N, 4.99.



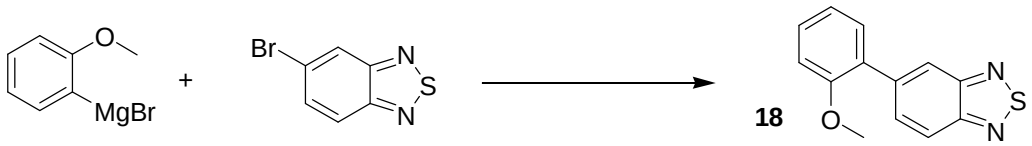
16

In a glove-box, a 200 mL round bottom flask equipped with a stir-bar was charged with NaH (1.21 g, 47.9 mmol). The flask was sealed with a septum and removed from the glove-box. The flask was equipped with a reflux condenser under an inert atmosphere. To the flask was added THF (50 mL). A solution of the aryl alcohol dissolved in THF (20 mL) was added dropwise. When effervescence ceased, a solution of complex **1** (591 mg, 2 mol %) dissolved in THF (3 mL) was via syringe, followed by the Grignard reagent (56.6 mmol, 1.3 Eq). The resulting mixture was allowed to stir for 16h at 70^{o}C. Following the typical work-up, the unpurified material was obtained as a solution in 620 mL of diethyl ether. For ease of purification, a portion of this crude sample (120 mL) was concentrated and purified to obtain a representative yield for the whole. 6-mesitylnaphthalen-2-ol; **16** (1.88 g, 85%) was isolated as a slightly yellow solid. M.p. =

45-47°C; R_f = 0.40 (diethyl ether/pentane, 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) d: 7.76 (d, *J* = 8.6 Hz, 2H), 7.56 (s, 1H), 7.26 (d, *J* = 7.5 Hz, 2H), 7.15 (d, J = 8.5 Hz, 1H), 7.00 (s, 2H), 5.08 (s, 1H), 2.38 (s, 3H), 2.06 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) APT d: 153.3 (+), 138.9 (+), 136.4 (+), 133.3 (+), 129.8 (-), 129.0 (+), 128.7 (-), 128.1 (-), 127.8 (-), 126.4 (-), 117.8 (-), 109.4 (-), 21.1 (-), 20.8 (-); Anal. Calcd. for $C_{19}H_{18}O$: C, 86.99; H, 6.92; O, 6.10. Found: C, 86.95; H, 6.92; O, 6.13.

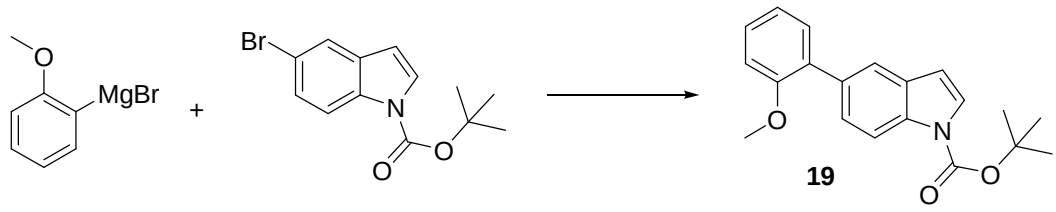


Following *Procedure A* at RT, 2-phenylthiophene **(17)** (48.1 mg, 60%) was prepared from 0.65 mmol of Grignard reagent and 0.5 mmol of aryl bromide, and isolated as a viscous, clear oil; R_f = 0.3 (pentane). Spectral data was in agreement with the literature.[4]

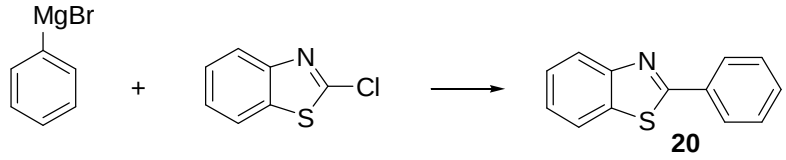


Following *Procedure B*, using complex **1** at RT, 5-(2-methoxyphenyl)benzo[*c*][1,2,5]thiadiazole **(18)** (89 mg, 74%) was prepared from 0.65 mmol of Grignard reagent and 0.5 mmol of aryl bromide, and isolated as a yellow, crystalline solid. M.p. = 82-85°C; R_f = 0.26 (diethyl ether/pentane, 5:95); ^{1}H NMR (400 MHz, $CDCl_3$) d: 8.12 (s, 1H), 8.03 (d, *J* = 9.1 Hz, 1H), 7.85 (d, *J* = 9.1 Hz, 1H), 7.44 (t, *J*

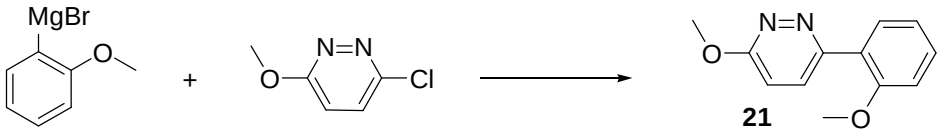
= 7.6, 2H), 7.05 (qn, *J* = 8.1 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) d: 156.6, 155.2, 154.1, 140.4, 132.6, 130.8, 129.8, 129.1, 121.1, 120.1, 111.5, 55.6; Anal. Calcd. for $C_{13}H_{10}N_2OS$: C, 64.44; H, 4.16; N, 11.56. Found: C, 64.77; H, 4.59; N, 11.29.



Following *Procedure A*, using complex **1** at RT, *tert*-butyl 5-(2-methoxyphenyl)-1*H*-indole-1-carboxylate **(19)** (537 mg, 83%) was prepared from 2.6 mmol of Grignard reagent and 2 mmol of aryl bromide, and isolated as a clear oil; R_f = 0.3 (diethyl ether/pentane, 3:97). Spectral data was in agreement with literature.[7]

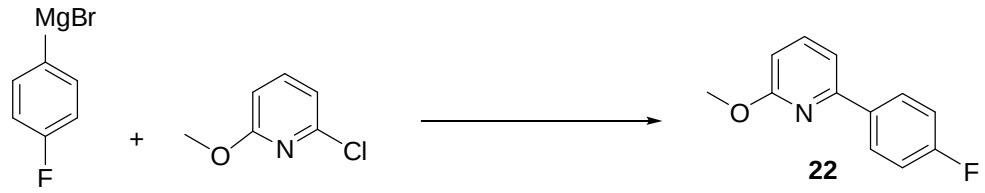


Following *Procedure A* at RT, 2-phenylbenzothiazole **(20)** (261 mg, 1.24 mmol, 62%) was prepared from 2.6 mmol of Grignard and 2 mmol of aryl chloride and isolated as a yellow crystalline solid. M.p. = 111-113^{o}C; Lit. m.p. = 113-114^{o}C;[1] R_f = 0.35 (diethyl ether/pentane, 4:96). Spectral data was in agreement with the literature.[1]



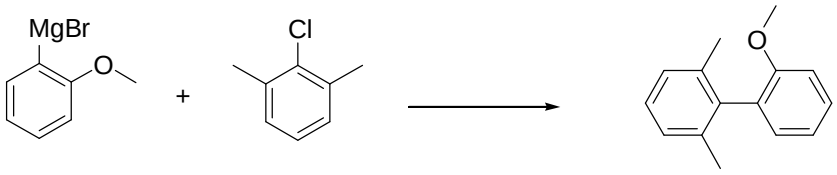
Following *Procedure A* at RT, 3-methoxy-6-(2-methoxyphenyl)pyridazine **(21)** (70.3 mg, 65%) was prepared from 0.65 mmol of Grignard and 0.5 mmol of aryl chloride and isolated as a beige crystalline solid. M.p. = 81-83^{o}C; R_f = 0.3 (diethyl ether/pentane,

3:97); ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.94 (t, *J* = 9.1 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 4.20 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) d: 163.7, 156.9, 154.6, 131.5, 130.9, 130.7, 125.7, 121.2, 116.3, 111.3, 55.6, 54.8; Anal. Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96; O, 14.80. Found: C, 66.56; H, 5.68; N, 12.63, O, 14.39.



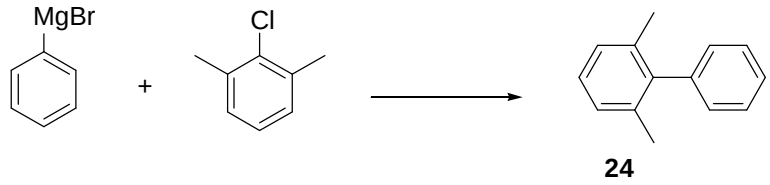
22

Following *Procedure A* at RT, 2-(4-fluorophenyl)-6-methoxypyridine (**22)** (128 mg, 0.63 mmol, 63%) was prepared from 1.5 mmol of Grignard and 1 mmol of aryl chloride and isolated as a yellow oil; R_f = 0.5 (diethyl ether/pentane, 3:97); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (t, *J* = 6 Hz, 2H,), 7.64 (t, *J* = 8 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 1H) 4.01(s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) d: 164.7, 163.8, 162.2, 153.7, 139.3, 135.2, 128.5 (d, $J_{C\text{-}F}$ = 9.1 Hz), 115.6, 115.4, 112.4, 109.2, 53.2; Anal. Calcd. for $C_{12}H_{10}FNO$: C, 70.93; H, 4.96; N, 6.89. Found: C, 70.56; H, 5.15; N, 6.68.

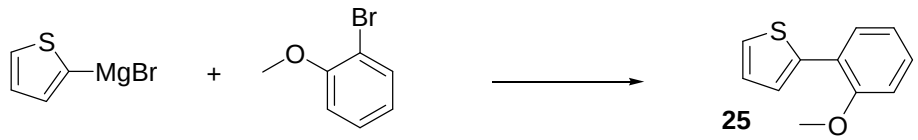


23

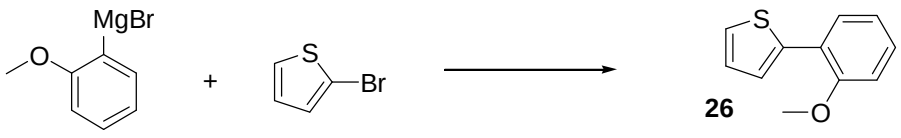
Following *Procedure A*, 2-(2-methoxyphenyl)-1,3-dimethylbenzene **(23)** (115 mg, 54%) was prepared from 1.3 mmol of Grignard reagent and 1 mmol of aryl halide, and isolated as a colorless oil; R_f = 0.4 (diethyl ether/pentane, 5:95). Spectral data was in agreement with literature.[9]



Following *Procedure A* at RT, 2,6-dimethylbiphenyl **(24)** (237 mg, 65%) was prepared from 2.6 mmol of Grignard reagent and 2 mmol of aryl chloride, and isolated as a colorless oil; R_f = 0.4 (pentane). Spectral data was in agreement with literature.[8]

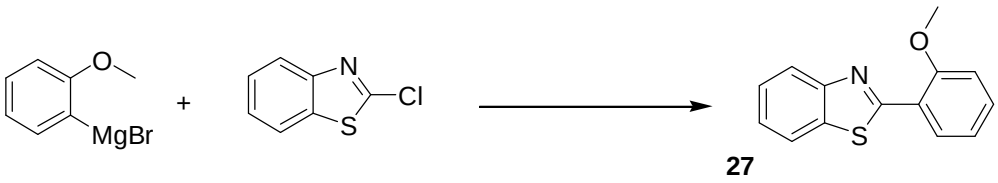


Following *Procedure B*, using complex **1**, 2-(2-methoxyphenyl)thiophene **(25)** (82.3 mg, 87%) was prepared from 0.65 mmol of Grignard reagent and 0.5 mmol of aryl bromide with LiCl additive (55 mg, 2.6 Eq.), and isolated as a viscous, yellow oil; R_f = 0.4 (diethyl ether/pentane, 5:95). Spectral data was in agreement with the literature.[3]



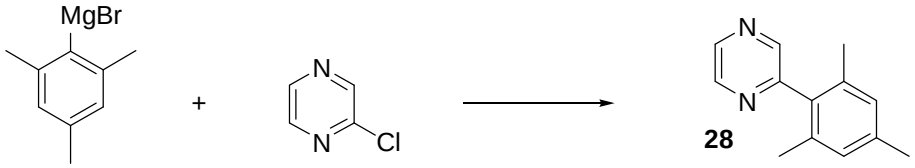
Following *Procedure B*, using complex **1** at 60°C, 2-(2-methoxyphenyl)thiophene **(26)** (82.3 mg, 91%) was prepared from 0.8 mmol of Grignard reagent and 0.5 mmol of aryl

bromide, and isolated as a viscous, yellow oil; R_f = 0.4 (diethyl ether/pentane, 5:95). Spectral data was in agreement with the literature.[3]



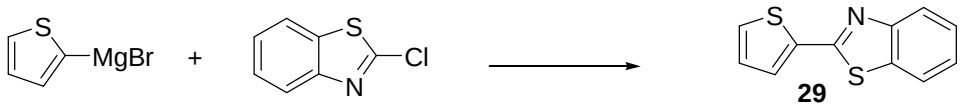
27

Following *Procedure B*, using complex **1**, 2-(2-methoxyphenyl)benzothiazole **(27)** (105 mg, 87%) was prepared from 0.65 mmol Grignard and 0.5 mmol of aryl halide, and isolated as a yellow, crystalline solid. M.p. = 95-98^{o}C; R_f = 0.2 (ethyl acetate/hexanes, 3:97); ^{1}H NMR (300 MHz, $CDCl_3$) d: 8.56 (d, *J* = 7.6 Hz, 1H), 8.12 (d, *J* = 7.9 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.54-7.37 (m, 3H), 7.19-7.08 (m, 2H), 4.08 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) d: 191.9, 163.1, 157.2, 152.2, 136.1, 131.7, 129.5, 125.8, 124.6, 122.8, 121.2, 111.7; Anal. Calcd. for $C_{14}H_{11}NOS$: C, 69.68; H, 4.59; N, 5.80; O, 6.63. Found: C, 69.55; H, 4.54; N, 5.78.

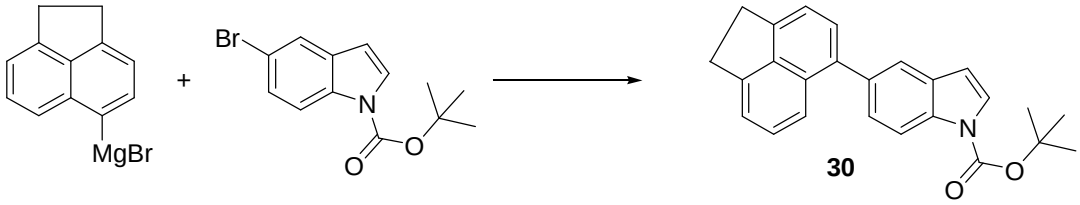


28

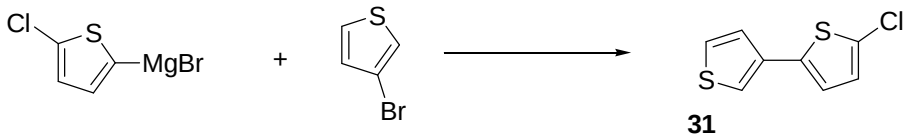
Following *Procedure C* using complex **1**, 2-mesitylpyrazine **(28)** (85.3 mg, 86%) was prepared from 0.8 mmol of Grignard reagent and 0.5 mmol of aryl chloride, and isolated as a clear, yellow oil; R_f = 0.2 (diethyl ether/pentane, 20:80); ^{1}H NMR (300 MHz, $CDCl_3$) d: 8.71 (s, 1H), 8.54 (s, 2H), 6.98 (s, 2H), 2.34 (s, 3H), 2.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) d: 155.9, 146.0, 144.4, 142.5, 138.4, 136.1, 134.0, 128.6, 21.1, 20.1; Anal. Calcd. for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.33; H, 7.43; N, 14.68.



Following *Procedure C*, using complex **1** at RT, 2-(thiophen-2-yl)benzothiazole **(29)** (91.8 mg, 85%) was prepared from 0.8 mmol of Grignard reagent and 0.5 mmol of aryl chloride, and isolated as a viscous, brown oil; R_f = 0.3 (diethyl ether/pentane, 5:95). Spectral data was in agreement with literature.[1]

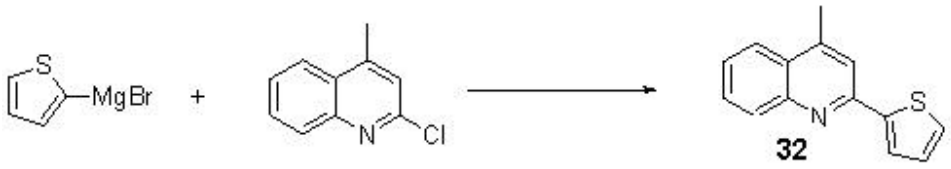


Following *Procedure C* using complex **1** at RT, *tert*-butyl 5-acenaphthyl-1*H*-indole-1-carboxylate **(30)** (142.2 mg, 77%) was prepared from 0.8 mmol of Grignard and 0.5 mmol of aryl bromide and isolated as a yellow, viscous oil; R_f = 0.3 (diethyl ether/pentane, 1:99); ^{1}H NMR (400 MHz, $CDCl_3$) d: 8.33 (d, *J* = 7.3 Hz, 1H), 7.81 (s, 2H), 7.75 (s, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 7.0 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.40 (dd, *J* = 16.9, 6.9 Hz, 2H), 6.71 (s, 1H), 3.50 (s, 4H), 1.79 (s, 9H); ^{13}C NMR (100.6 MHz, $CDCl_3$) APT d: 149.9, 146.2, 145.3, 139.7, 136.0, 135.1, 134.4, 130.9, 130.1, 128.8, 128.0, 126.5, 122.0, 121.1, 119.4, 119.2, 115.0, 107.6, 83.8, 30.6, 30.1, 28.3; Anal. Calcd. for $C_{25}H_{23}NO_2$: C, 81.27; H, 6.27; N, 3.79. Found: C, 81.16; H, 6.17; N, 3.44.



31

Following *Procedure C*, using complex **1**, 3-(5-chlorothiophen-2-yl)thiophene **(31)** (85 mg, 85%) was prepared from 0.8 mmol of Grignard reagent and 0.5 mmol of aryl bromide, and isolated as a beige solid. M.p. = 74-77^{o}C; R_f = 0.65 (pentane); ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.37 (d, *J* = 4.4 Hz, 1H), 7.34 (s, 1H), 7.25 (d, *J* = 4.8 Hz, 1H), 6.98 (d, *J* = 3.2 Hz, 1H), 6.87 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) APT d: 137.8 (+), 134.8 (+), 128.2 (+), 126.8 (+), 126.6 (-), 125.6 (-), 122.3 (-), 119.8(-); Anal. Calcd. for $C_8H_5ClS_2$: C, 47.87; H, 2.51. Found: C, 47.80; H, 2.31.

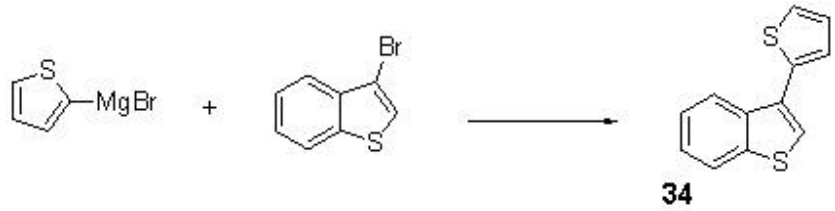


32

Following *Procedure C* using complex **1**, 4-methyl-2-(thiophen-2-yl)quinoline **(34)** (94.6 mg, 84%) was prepared from 0.8 mmol of Grignard reagent and 0.5 mmol of aryl chloride, and was isolated as a viscous, yellow oil; Rf = 0.3 (diethyl ether/pentane, 2:98). ^{1}H NMR (300 MHz, $CDCl_3$) d: 8.12 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.74-7.63 (m, 3H), 7.50-7.47 (m, 2H), 7.16 (t, *J* = 3.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d: 152.0, 147.9, 145.5, 144.6, 129.8, 129.4, 128.3, 127.9, 127.3, 125.8, 125.6, 123.6, 118.2, 18.8.

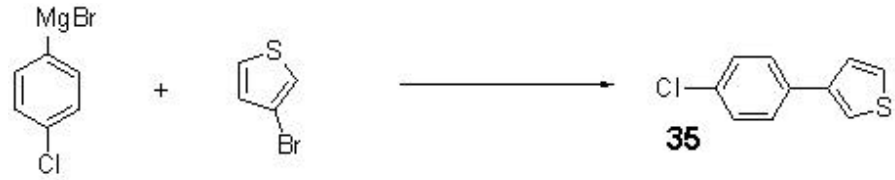
33

Following *Procedure C*, using complex **1** at RT, 2-(4-methoxyphenyl)thiophene **(33)** (63.2 mg, 67%) was prepared from 0.8 mmol of Grignard reagent and 0.5 mmol aryl chloride, and isolated as a white solid. M.p. = 105°C; Lit. m.p. = 103-104°C;[5] R_f = 0.3 (diethyl ether/pentane, 2:98). Spectral data was in agreement to literature values.[5,6]



34

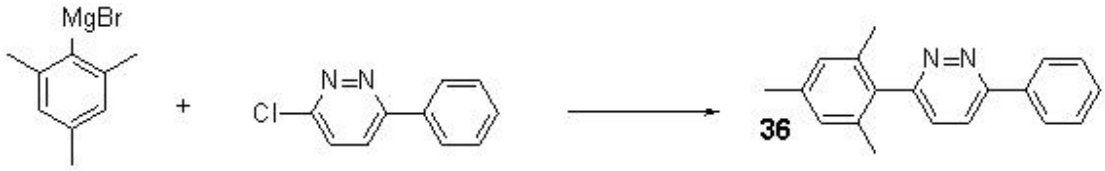
Following *Procedure C* using complex **1**, 3-(thiophen-2-yl)benzo[*b*]thiophene **(34)** (80 mg, 76%) was prepared from 0.8 mmol of Grignard reagent and 0.5 mmol of aryl chloride, and was isolated as a viscous, green oil; Rf = 0.4 (pentane). ^{1}H NMR (300 MHz, $CDCl_3$) d: 8.21 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 7.4 Hz, 1H), 7.56 (s, 1H), 7.49 (qn, *J* = 7.7 Hz, 2H), 7.43-7.40 (m, 2H), 7.23 (t, *J* = 3.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) d: 140.6, 137.5, 137.4, 130.7, 127.5, 125.2, 124.8, 124.7, 124.6, 123.9, 123.0, 122.9.



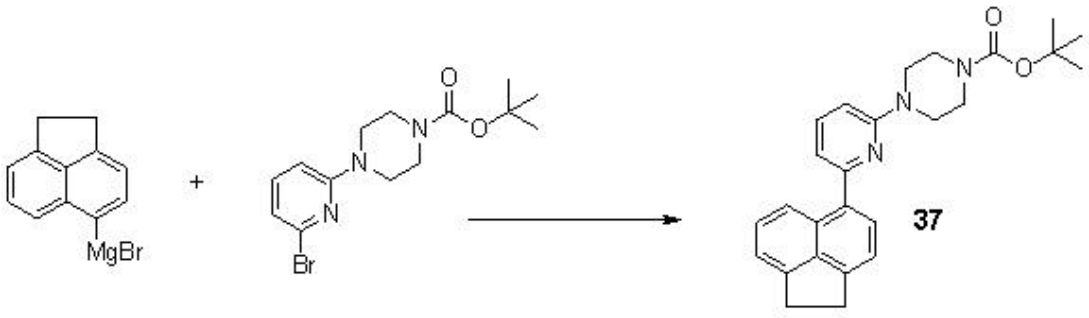
35

Following *Procedure C* using complex **1**, 3-(4-chlorophenyl)thiophene **(35)** (508 mg, 87%) was prepared from 3.6 mmol of Grignard reagent and 3.0 mmol of aryl bromide, and was isolated as a white solid. M.p. = 93-95°C; Rf = 0.4 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.55 (d, *J* = 8.4 Hz, 2H), 7.45 (s, 1H), 7.44-7.38 (m, 4H); ^{13}C NMR

(100.6 MHz, $CDCl_3$) APT d: 141.1 (-), 134.3 (-), 132.9 (-), 129.0 (+), 127.7 (+), 126.6 (+), 126.1 (+), 120.6 (+); Anal. Calcd. for $C_{10}H_7ClS$: C, 61.69; H, 3.62; Cl, 18.21; S, 16.47.



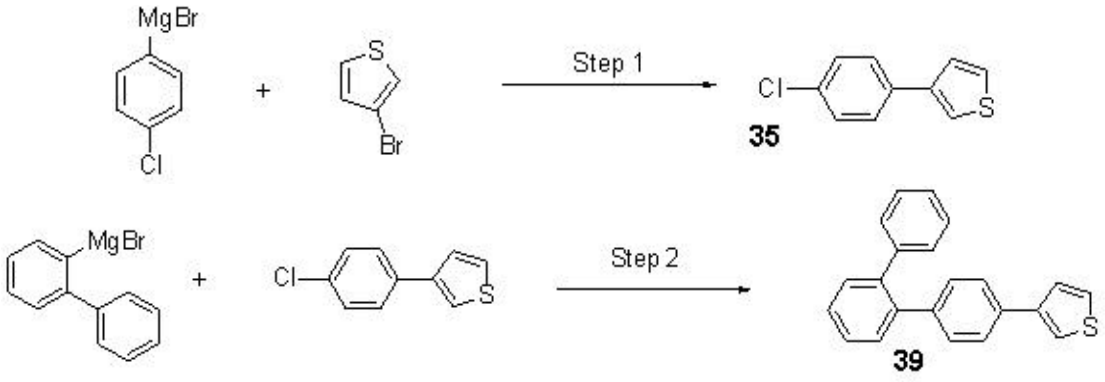
Following *Procedure C*, using complex **1** at RT, 3-mesityl-6-phenylpyridazine **(36)** (110 mg, 80%) was prepared from 0.8 mmol of Grignard reagent and 0.5 mmol of aryl chloride, and isolated as white solid. M.p. = 96-99^{o}C; R_f = 0.3 (diethyl ether/pentane, 25:75); ^{1}H NMR (300 MHz, $CDCl_3$) d: 8.21 (d, *J* = 7.3 Hz, 2H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.61-7.46 (m, 4H), 7.01 (s, 2H), 2.38 (s, 3H), 2.11 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) d: 160.6, 157.3, 138.4, 136.2, 136.3, 136.1, 134.4, 130.0, 129.0, 128.6, 127.1, 123.6, 21.1, 20.3; Anal. Calcd. for $C_{19}H_{18}N_2$: C, 83.18; H, 6.61; N, 10.21. Found: C, 82.91; H, 6.85; N, 10.14.



Following *Procedure C* using complex **1** at RT, 4-Boc-(6-acenaphthyl-2-pyridyl)piperazine **(37)** (86 mg, 83%) was prepared from 0.4 mmol of Grignard and 0.25 mmol of aryl bromide and isolated as a yellow, crystalline solid. M.p. = 145-147^{o}C; R_f = 0.3 (diethyl ether/pentane, 20:80); ^{1}H NMR (400 MHz, $CDCl_3$) d: 8.15 (d, *J* = 8.4 Hz,

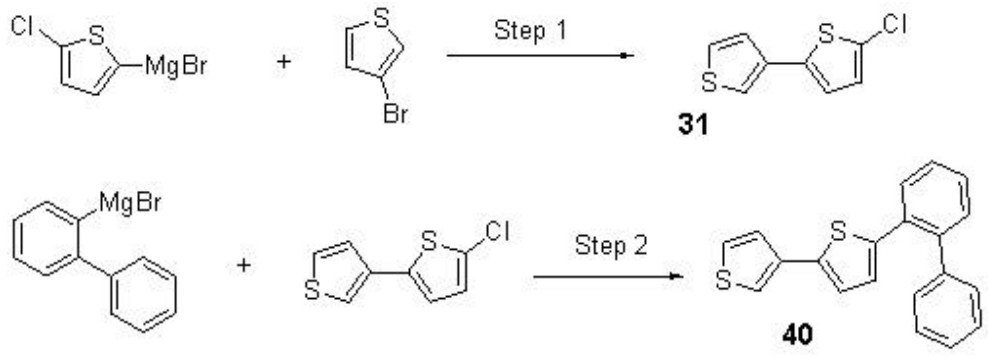
1H), 7.71 (d, *J* = 7.1 Hz, 1H), 7.64 (t, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.35 (q, *J* = 7.1 Hz, 2H), 7.05 (d, *J* = 7.4, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 3.64 (d, *J* = 16 Hz, 8H), 3.46 (s, 4H), 1.53 (s, 9H); ^{13}C NMR (100.6 MHz, $CDCl_3$) APT d: 158.8, 157.1, 154.9, 146.8, 146.1, 139.8, 138.0, 134.4, 129.5, 129.1, 128.0, 121.4, 119.3, 119.0, 114.1, 104.9, 79.9, 45.1, 30.5, 30.1, 28.5; Anal. Calcd. for $C_{26}H_{29}N_3O_2$: C, 75.15; H, 7.03; N, 10.11; O, 7.70. Found: C, 75.38; H, 7.13; N, 9.86; O, 7.44.

Following *Procedure C* using complex **1**, 3-mesitylthiophene **(38)** (80 mg, 76%) was prepared from 0.8 mmol of Grignard reagent and 0.5 mmol of aryl bromide, and was isolated as a viscous, clear oil; Rf = 0.7 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.41 (d, *J* = 7.3 Hz, 1H), 7.05 (s, 1H), 6.96 (s, 1H), 2.36 (s, 3H), 2.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) d: 140.7, 136.9, 136.8, 133.9, 129.0, 128.0, 125.0, 122.2, 21.0, 20.6; Anal. Calcd. for $C_{13}H_{14}S$: C, 77.18; H, 6.97.



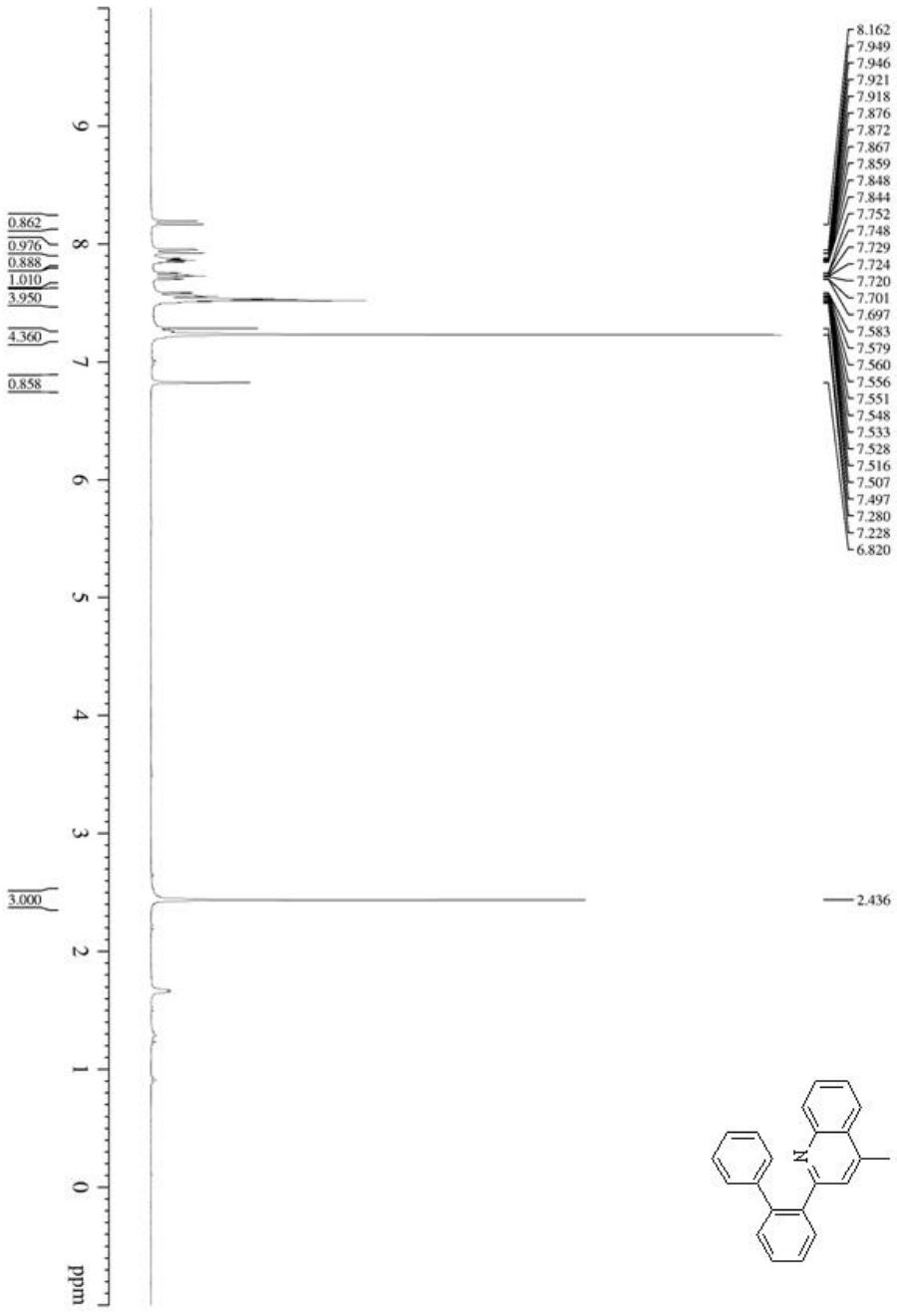
Following *Tandem Procedure* using complex **1**, 3-(4-biphenylylphenyl)thiophene **(39)** (246 mg, 79%) was prepared from 0.6 mmol of the first Grignard reagent, 0.8 mmol of

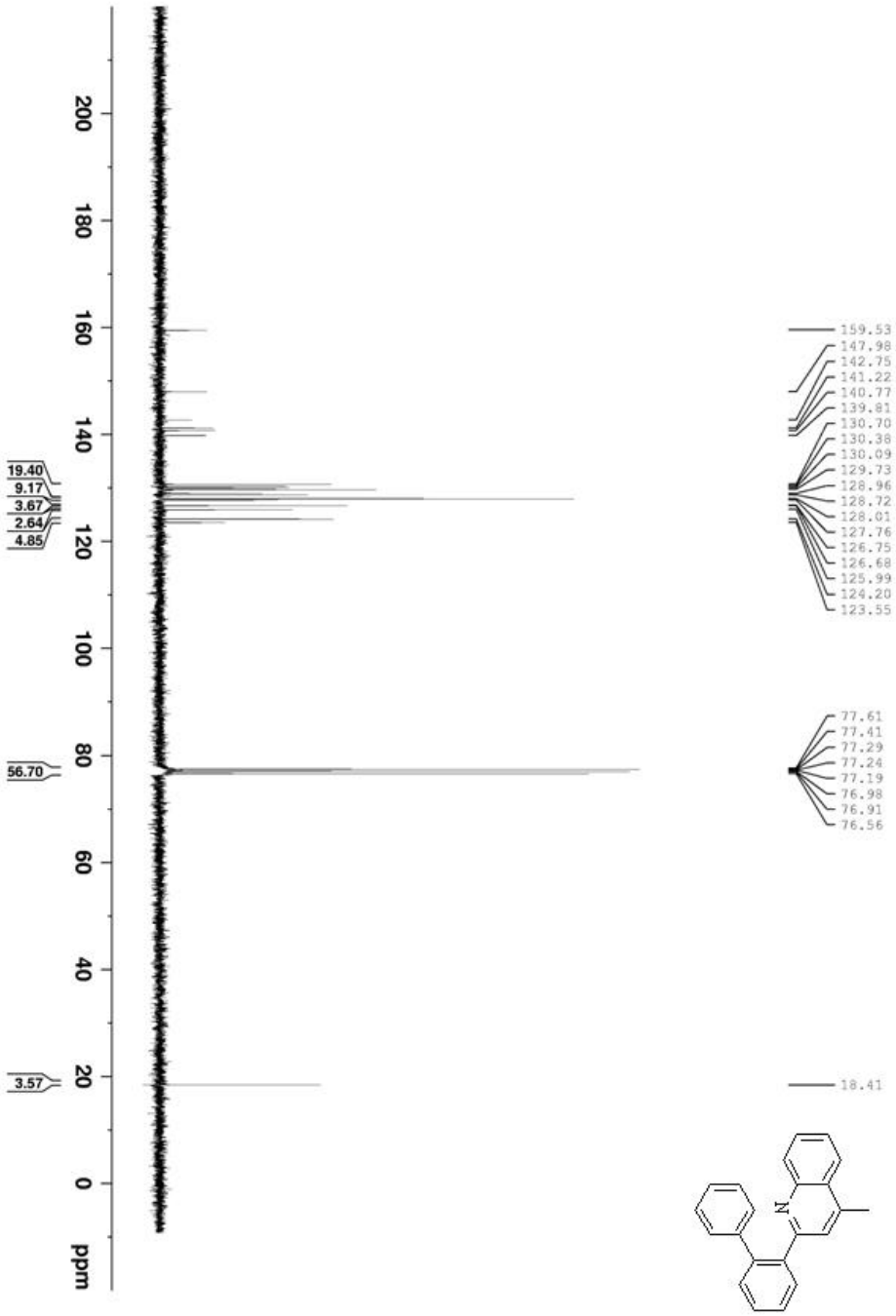
the second Grignard reagent and 0.5 mmol of aryl bromide, and was isolated as a white solid; Rf = 0.3 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.52-7.48 (m, 7H), 7.42 (s, 2H), 7.29-7.22 (m, 7H), 7.29 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) APT d: 141.9 (-), 141.5 (-), 140.6 (-), 140.4 (-), 140.1 (-), 133.8 (-), 130.8 (+), 130.6 (+), 130.4 (+), 129.9 (+), 128.0 (+), 127.6 (+), 126.5 (+), 126.2 (+), 125.9 (+), 120.1 (+); Anal. Calcd. for $C_{22}H_{16}S$: C, 84.57; H, 5.16; S, 10.26.



Following *Tandem Procedure*, using complex **1**, 2-(biphenylylthiophen-3-yl)thiophene **(40)** (99 mg, 62%) was prepared from 0.6 mmol of the first Grignard reagent, 0.8 mmol of the second Grignard reagent and 0.5 mmol of aryl bromide, and isolated as a beige solid. M.p. = 69-71^{o}C; R_f = 0.40 (pentane); ^{1}H NMR (300 MHz, $CDCl_3$) d: 7.65 (s, 1H), 7.45 (s, 3H), 7.37-7.34 (m, 7H), 7.29 (s, 1H), 7.01 (s, 1H), 6.61 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) APT d: 141.6 (+), 140.8 (+), 139.1 (+), 135.6 (+), 133.0 (+), 131.0 (-), 130.3 (-), 129.7 (-), 129.7 (-), 128.27 (-), 127.8 (-), 127.6 (-), 127.1 (-), 126.3 (-), 125.9 (-), 123.3 (-), 119.3 (-); Anal. Calcd. for $C_{20}H_{14}S_2$: C, 75.43; H, 4.43; S, 20.14. Found: C, 75.79; H, 4.42; S, 19.79.

^{1}H-NMR and ^{13}C-NMR Spectra

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80
60
40
20
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56.70
3.57
159.53
147.98
142.75
141.22
140.77
139.81
130.70
130.38
130.09
129.73
128.96
128.72
128.01
127.76
126.75
126.68
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124.20
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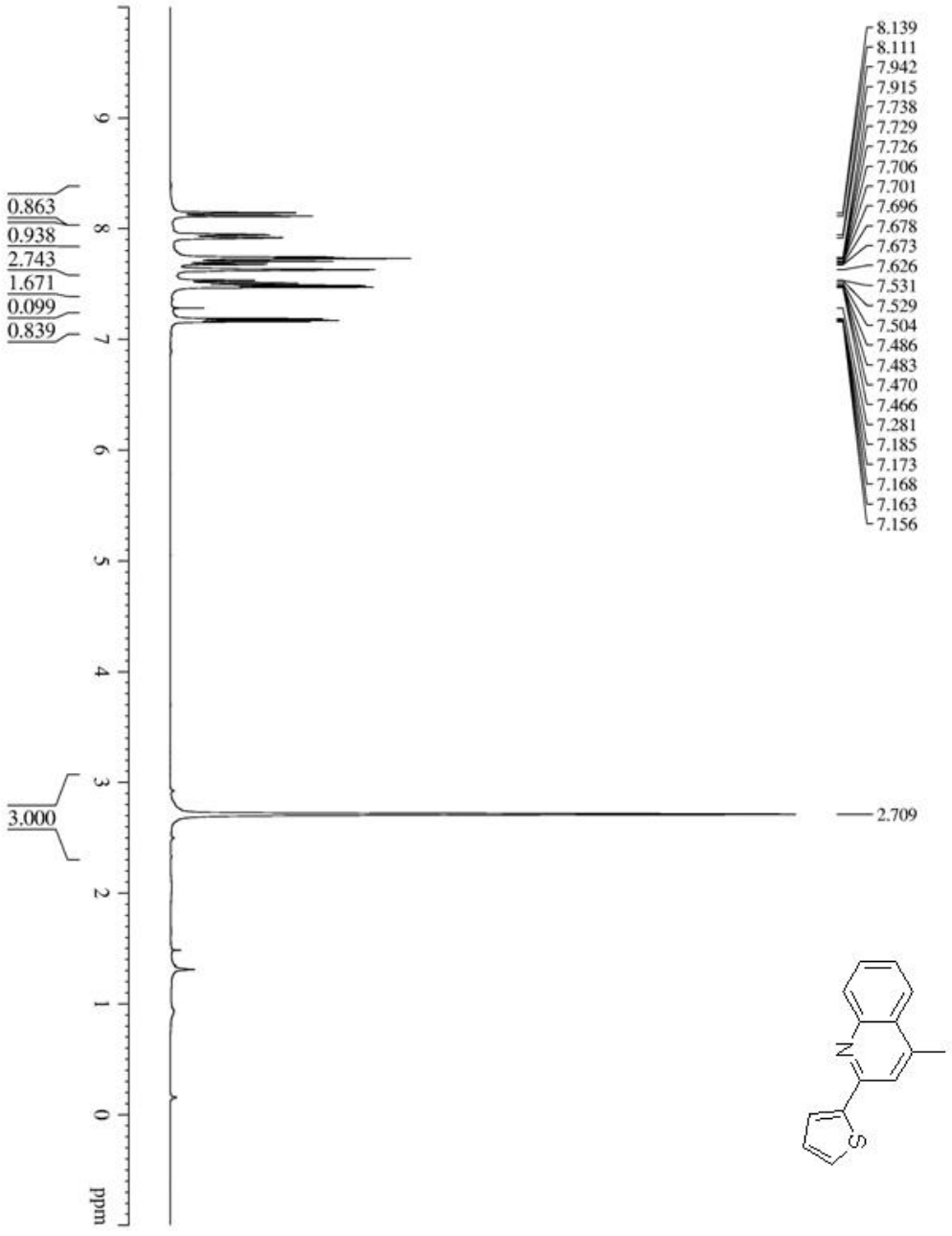
76.91
76.56
18.41
N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7.531
7.529
7.504
7.486
7.483
7.470
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7.281
7.185
7.173
7.168
7.163
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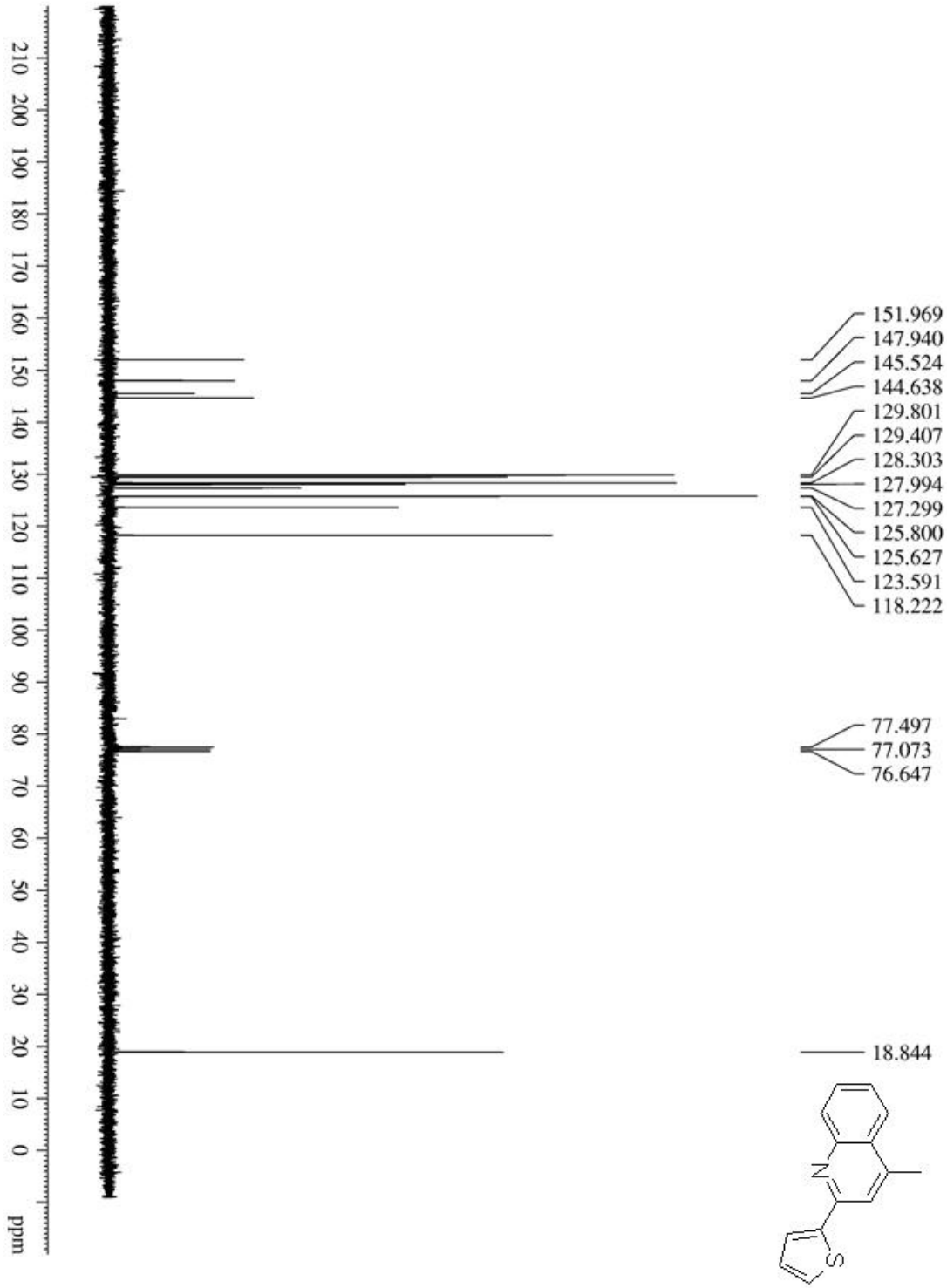
ppm
N
S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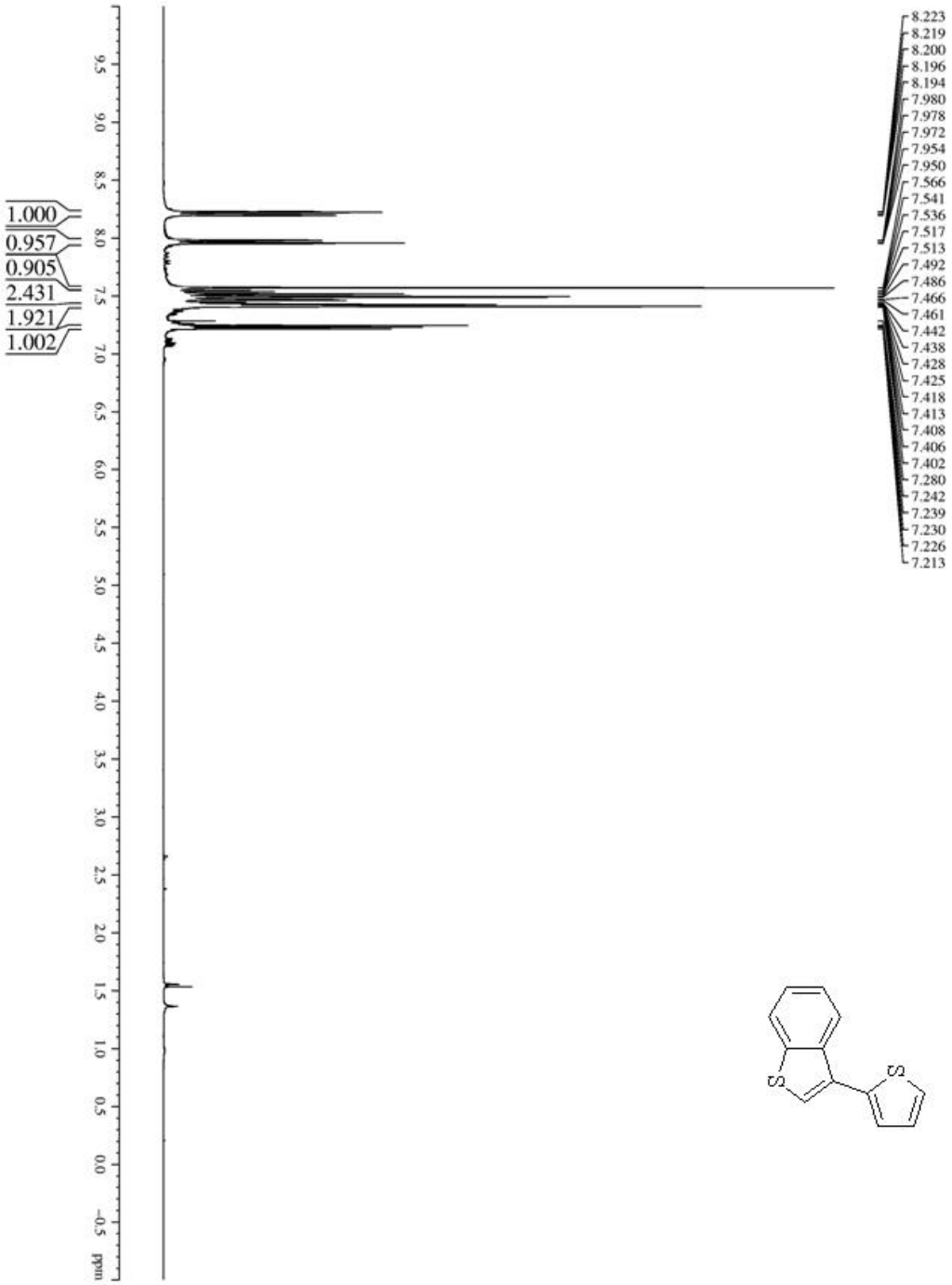
18.844
N
S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7.541
7.536
7.517
7.513
7.492
7.486
7.466
7.461
7.442
7.438
7.428
7.425
7.418
7.413
7.408
7.406
7.402
7.280
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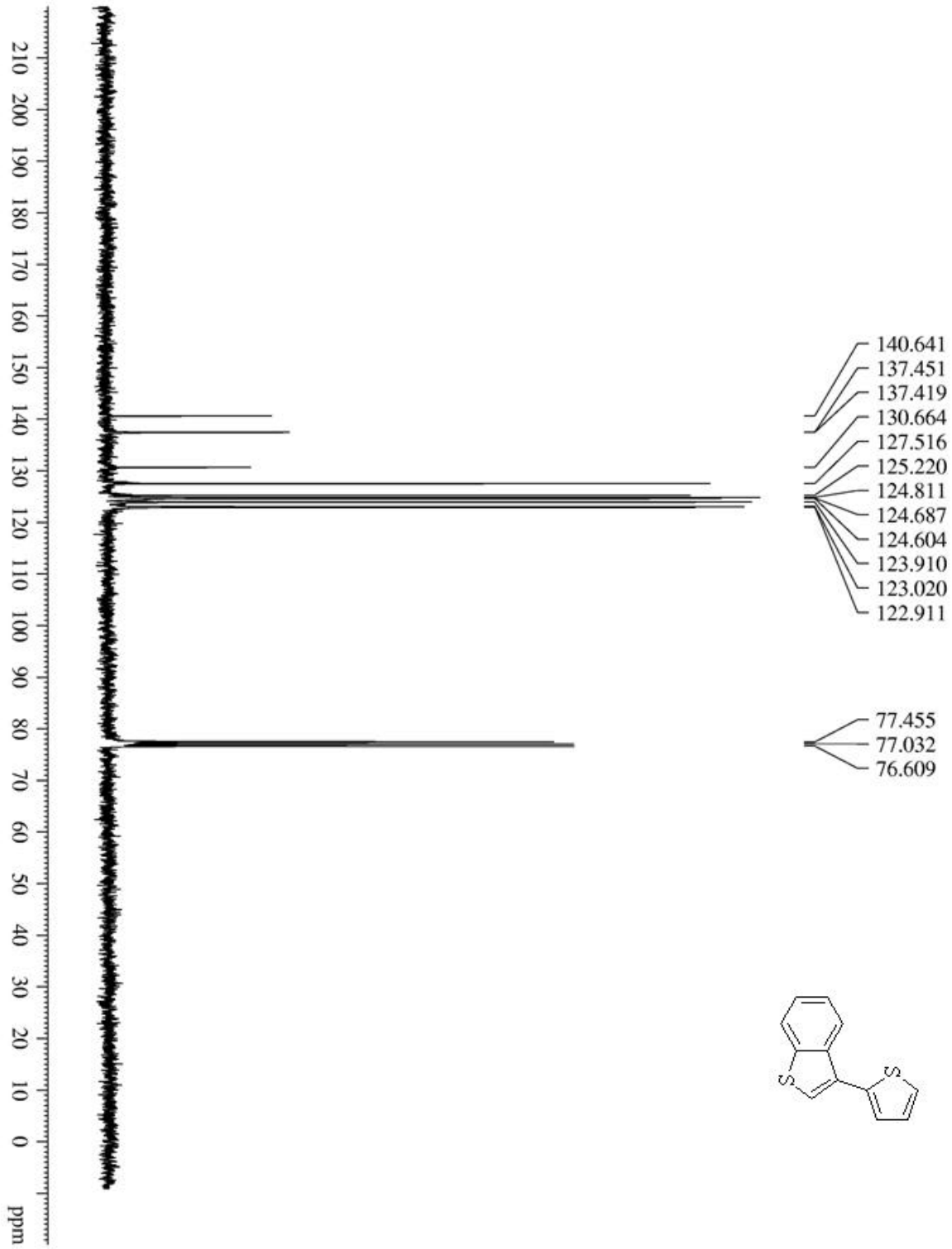
ppm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122.911
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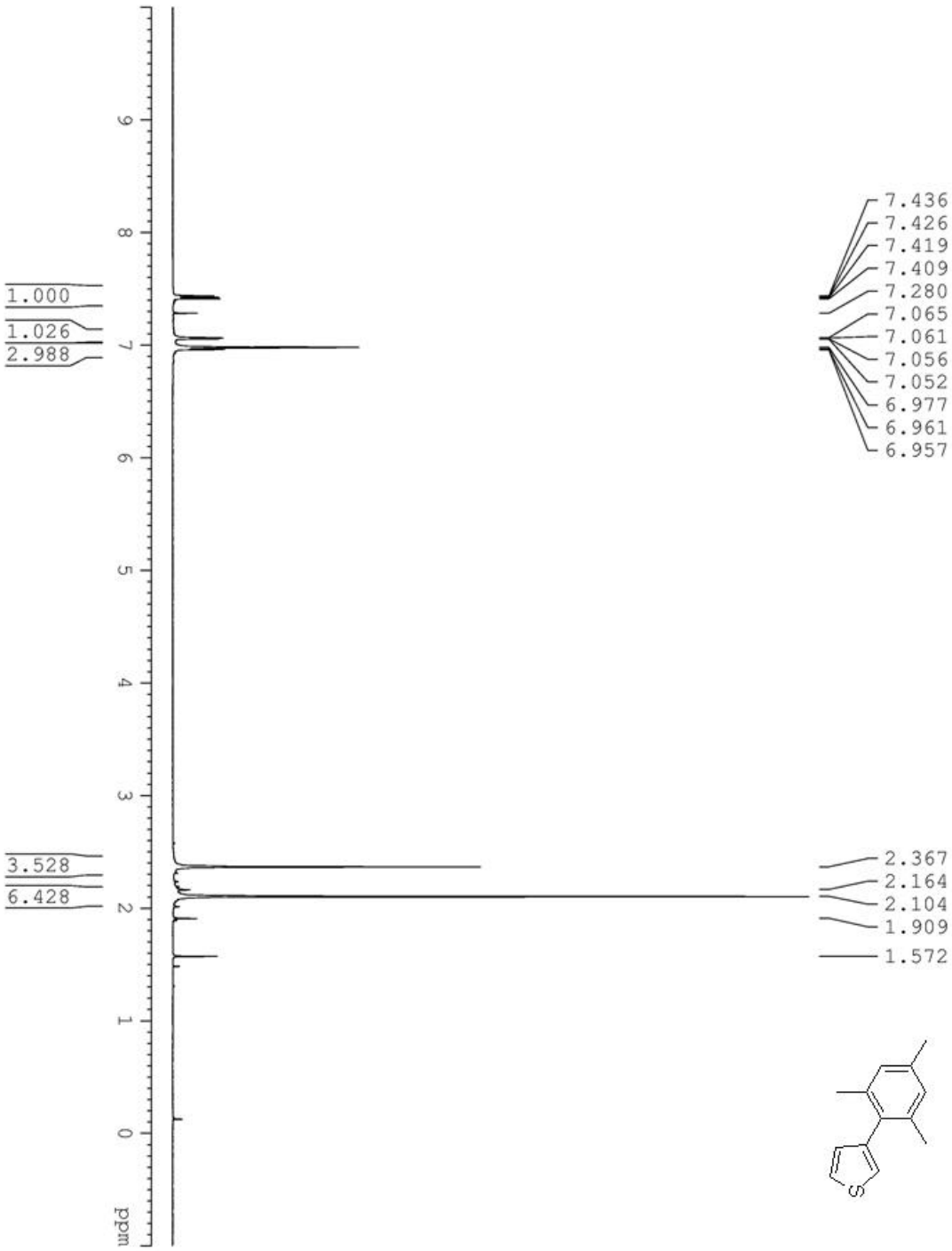
77.032
76.609
S
S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7.056
7.052
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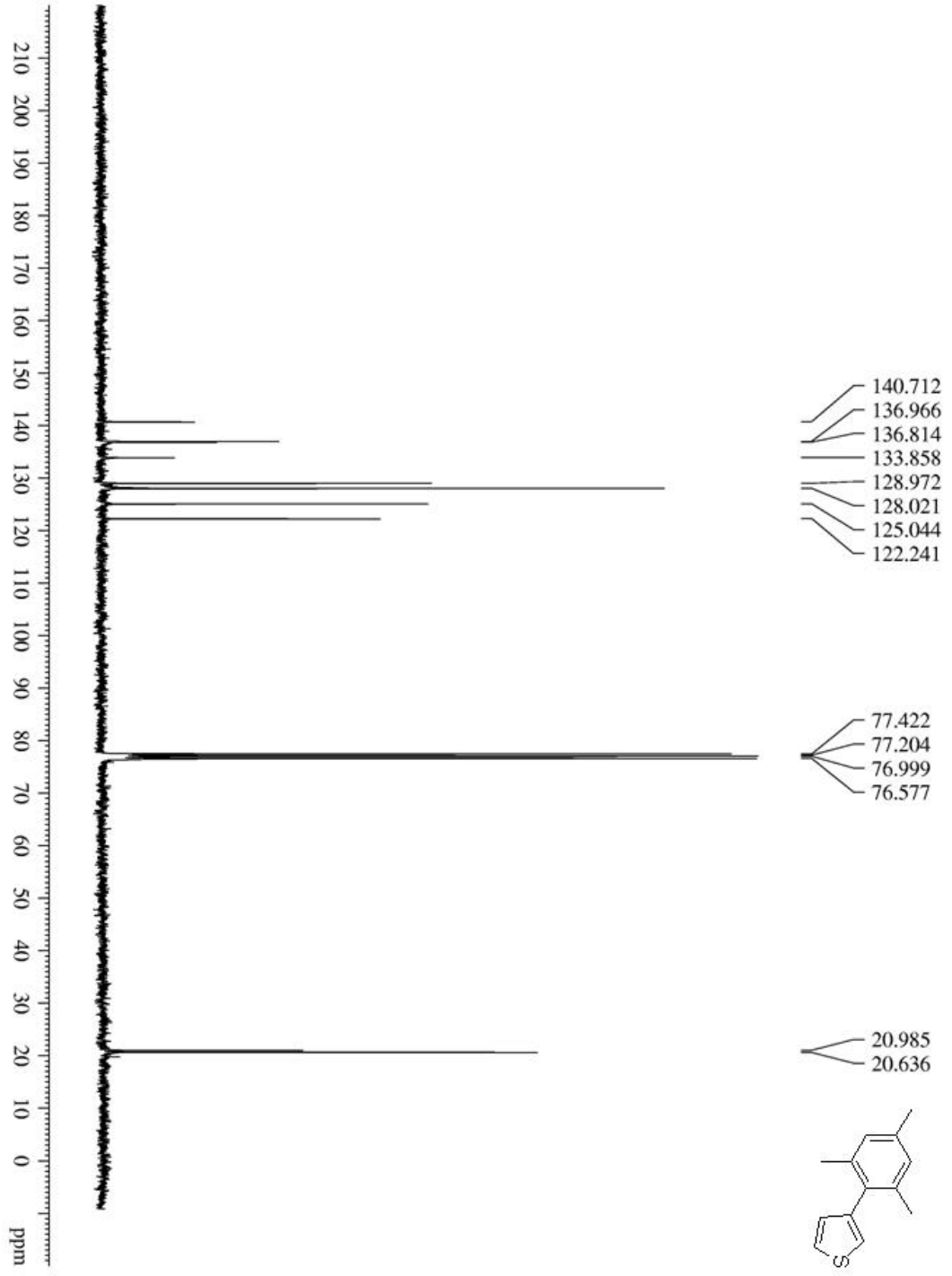
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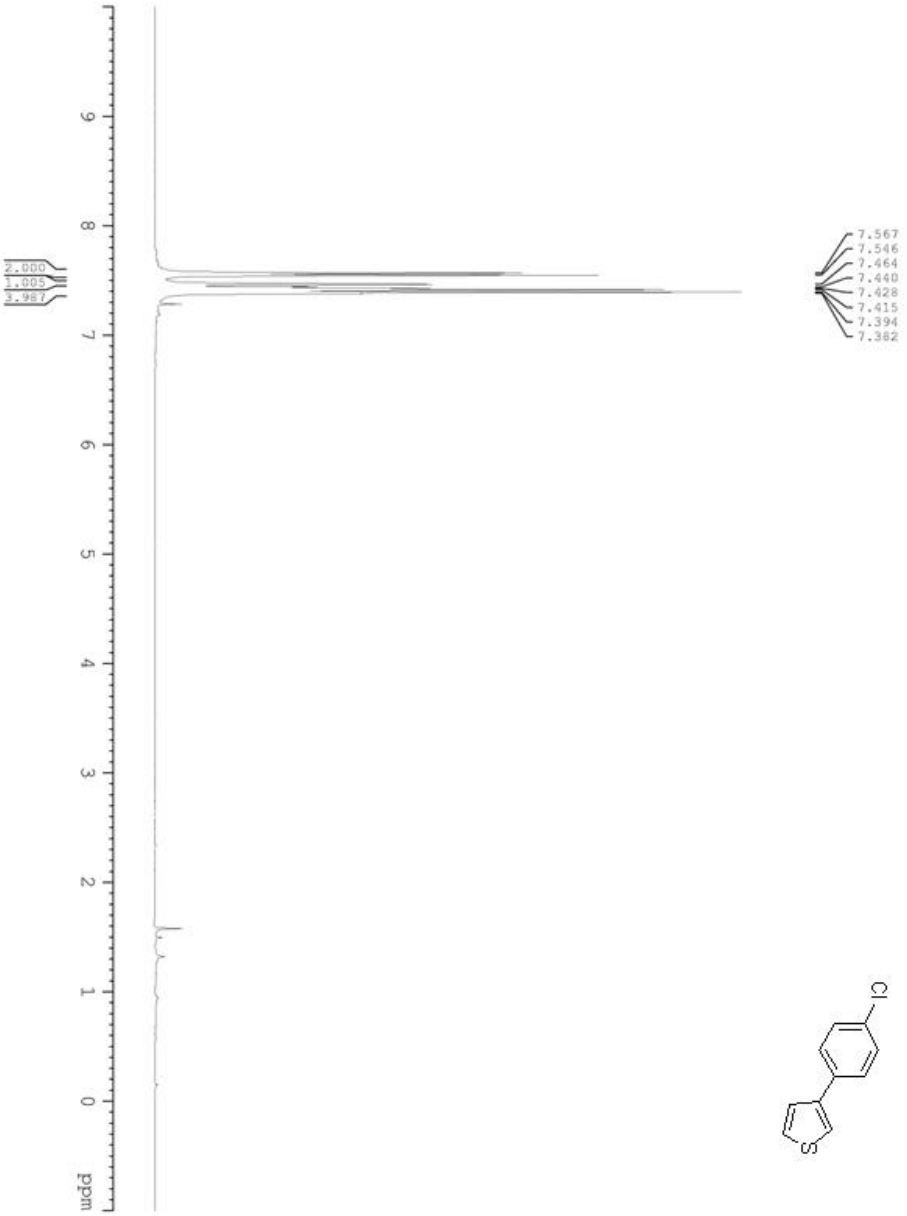
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O
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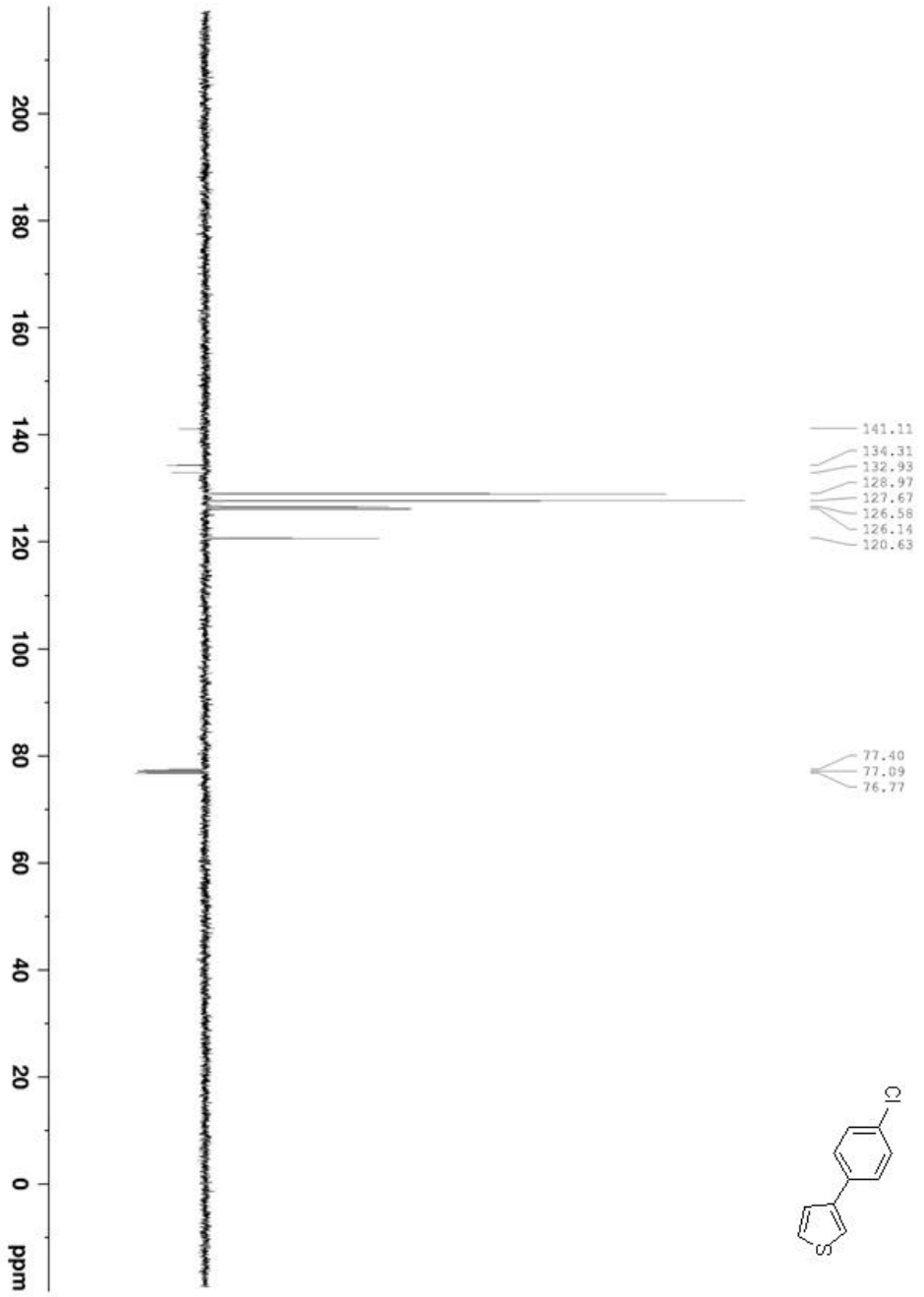
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60
40
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126.14
120.63
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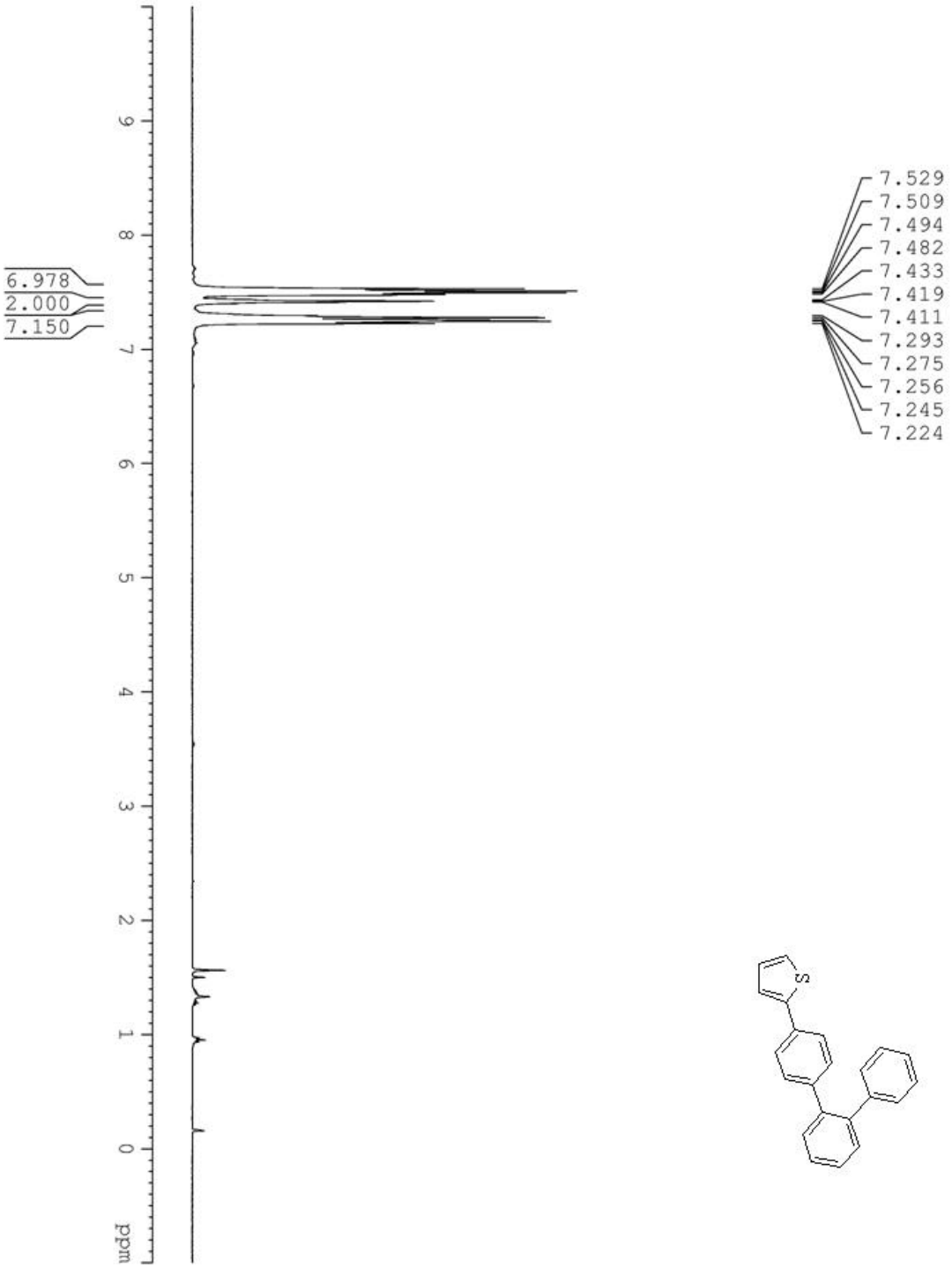
76.77
Cl
O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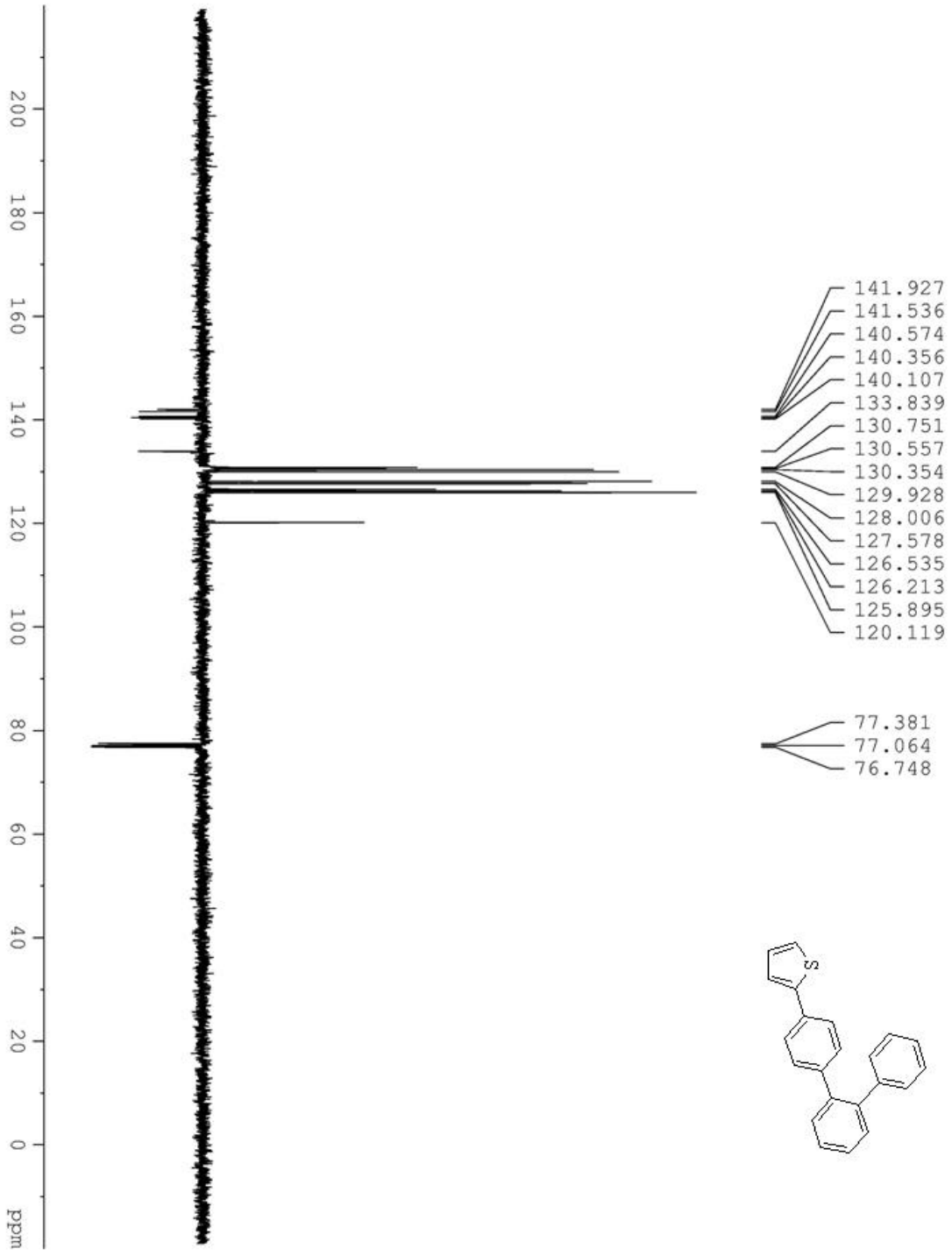
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126.535
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125.895
120.119
77.381
77.064
76.748
S

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