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Supporting Information

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Microwave-Promoted Rhodium-Catalyzed Arylation of Heterocycles via C-H Bond Activation

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General Experimental

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Technical Phobane (ca. 1:1 mixture of 9-H-bicyclo-[4.2.1]-9-phosphanonane and 9-H-bicyclo-[3.3.1]-9-phosphanonane) was obtained from Digital Specialty chemicals. Molecular sieves (3 Å) and basic alumina (activity I) were heated at 250 °C under 0.5 mm Hg vacuum overnight to remove any traces of water. Tetrahydrofuran (THF) and methylene chloride were passed through columns of activated alumina (type A2, size 12 x 32, Purify Co.) under nitrogen pressure, sparged with N_2, and stored over molecular sieves prior to use. Dichlorobenzene (DCB) was stirred over NaH overnight, distilled at 20 mm Hg, and stored over 3 Å molecular sieves. THF-d_8 was stirred under nitrogen over sodium/benzophenone ketyl, vacuum transferred into a sealable storage vessel, degassed using three consecutive freeze pump thaw cycles, and stored over activated 3 Å molecular sieves. Benzene-d_6 was transferred into a sealable storage vessel, degassed using three consecutive freeze pump thaw cycles, and stored over activated 3 Å molecular sieves. Triethylamine and diisopropylisobutylamine were stirred over CaH_2 overnight, distilled in vacuo or under nitrogen, degassed using three consecutive freeze pump thaw cycles, and stored over activated 3 Å molecular sieves. PhI was stirred over CaH_2 overnight and distilled from CaH_2 in vacuo. All reagents were degassed and handled under an inert nitrogen atmosphere using syringe and cannula techniques. Unless otherwise noted, all reactions were prepared in flame or oven-dried glassware in a nitrogen-filled Vacuum Atmospheres inert atmosphere box and performed in sealed vessels. Conventionally heated reactions were conducted as previously described.[1] Microwave reactions were conducted in either 2 mL or 5 mL microwave vials (Biotage No. 352016 or 351521) and heated in a Personal Chemistry Smith Synthesizer. Products were quantified by GC as previously described.[1] Flash column chromatography was carried out using a Biotage SP Flash Purification System (Biotage No. SP1-B1A) with Flash+ cartridges (Biotage No. FPK0-1107-16046, or FPL0-1118-15045)

using hexanes/ethyl acetate or water/acetonitrile gradients, respectively unless otherwise noted. NMR spectra (^{1}H, ^{13}C, and ^{31}P) were obtained on a Bruker AMX-400 spectrometer. Chemical shifts are reported in ppm, and coupling constants are reported in Hz. ^{1}H resonances are referenced to residual protonated solvent, while ^{31}P resonances are referenced to a trimethylphosphate external standard. ^{13}C NMR spectra are included for 2-arylimidazoles not reported in the literature. In some cases rapid tautomerization of the benzimidazole moiety apparently led to broadening and or absence of 1-2 of the expected ^{13}C resonances as has been previously reported.[2] Mass spectrometry was performed by the University of California, Berkeley mass spectrometry facility or by the GC/MS system described in ref. 1. Crystal structure data for **4a** and **4b** can be retrieved from the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC 291472 and 291473. Complete analytical data and synthesis procedures have been reported in the literature for $[RhCl(coe)_2]_2$ (also available from Strem),[3] 3,4-dihydroquinazoline,[1] 5-(4-fluoro-phenyl)-4-phenyl-1*H*-imidazole,[4] 5-(4-methoxy-phenyl)-4-phenyl-1*H*-imidazole,[5] and 3-phenyl-4*H*-[1,2,4]triazole.[6]

Separation of phobane iosomers. The separation was carried out as described by Pringle and co-workers with the following modifications.[7] All extractions described in the protocol were carried out in sealable glass vessels using Schlenk techniques to transfer the desired phase. The combined organic phases containing the separated phosphine isomers were concentrated in vacuo, brought into an inert atmosphere box, and filtered through basic alumina (activity I) to give the isomerically pure phosphines. The ^{31}P{^{1}H} NMR spectra for the isomerically pure phosphines matched those reported in the literature.[6]

Alkylation of phobane isomers, 2a.[8] 9-H-bicyclo-[4.2.1]-9-phosphanonane (2.00 g, 14.1 mmol) and 50 mL of diethyl ether were added to a 100 mL round-bottomed flask containing a stir bar. The flask was fit with a septum and removed from the inert atmosphere box. The solution was cooled to -30 °C and *n*-BuLi (6.5 mL of a 2.5 M ether solution, 15.5 mmol) was added dropwise via syringe over 20 minutes using a syringe pump. Following the addition, the reaction mixture was allowed to warm to room temperature over the course of an hour. The solution was cooled to 0 °C and cyclohexyl bromide (3.6

mL, 28.2 mmol) was added dropwise over 20 minutes using a syringe pump. The reaction mixture was allowed to warm to room temperature and stirred for 20 h. The solvent was removed in vacuo and the resulting yellow-white residue was distilled at 0.2 mm Hg using a Kugelrohr apparatus. A fraction, which contained distillate boiling up to 90 °C at 0.2 mm Hg, was discarded. A mixture of **2a** and **2b** was obtained as a colorless liquid with a boiling point of 115 °C at 0.2 mm Hg (1.26 g, 40%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.8-2.6 (m). $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6): δ 12.21, 9.50.

Significant amounts of an impurity were obtained if the distillation was conducted above 115 °C at 0.2 mm Hg. Small amounts of this impurity, up to 10% by $^{31}P\{^{1}H\}$ NMR spectroscopy (δ 14.68), were not detrimental to the efficiency of **2a/b** when used in the arylation reaction. The mixture could be further purified by chromatography of the corresponding borane adduct, followed by deprotection and redistillation of the phosphines as described below.

Preparation of 3a and 3b.[9] The mixture **2a/b** (0.10 g, 0.45 mmol) and methylene chloride (2.5 mL) were added to a 25 mL round bottomed flask containing a stir bar. The flask was fitted with a septum and a solution of BH_3 in THF (1.34 mL, 1M, 1.34 mmol) was added slowly via syringe. The flask was then removed from the inert atmosphere box and the mixture was stirred at room temperature for 4 h. The reaction mixture was then concentrated in vacuo to give a white solid. This material was dissolved in a minimal amount of methylene chloride, and a minimal amount of SiO_2 was added to give a powder after removal of the solvent in vacuo. The solid was loaded onto a wet SiO_2 column (25% CH_2Cl_2/hexanes) and eluted with the same solvent to give 0.28 g of **3a** (51%), $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6): δ 49.88, and 0.14 g of **3b** (28%), $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6): δ 45.93, as white solids.

Deprotection of 3a and 3b. A 25 mL oven-dried round bottomed flask containing a stir bar was fit with a septum and cooled under a stream of nitrogen. The appropriate borane adduct, eg. **3b** (0.141 g, 0.590 mmol), was added to the flask, and the flask evacuated and purged with nitrogen three times. Methylene chloride (3 mL) was added to the flask and the solution was cooled to 0 °C with stirring. A solution of HBF_4 in ether (0.30 g of a 54% solution, 1.8 mmol) was added dropwise to the cooled solution

over 5-10 minutes (gas evolved). Following the addition, the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was then slowly (ca. 1 min) transferred to a narrow Schlenk flask (6"x1") containing 20 mL of degassed (nitrogen sparged for 30 min) saturated $NaHCO_3$ (aq) via cannula (gas evolved). The mixture was gently, then vigorously shaken, and the layers were allowed to settle. The methylene chloride layer was removed using a syringe and added to a oven-dried Kontes bomb fit with a septum under nitrogen. The aqueous layer was extracted with 3x10 mL degassed methylene chloride in a similar fashion, and the organic fractions were combined. The septum was replaced with a Kontes stopper, and the solvent was removed in vacuo. The residue was filtered through a plug of alumina in an inert atmosphere box to provide 0.129 g (97%) of **2b** as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ 0.95 (m, 1H), 1.3-1.8 (m, 20H), 2.19 (m, 1H), 2.27 (m, 1H), 2.51 (m, 2H). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 9.57. HRMS-EI (m/z): $[M]^+$ calcd for $C_{14}H_{25}P$, 224.169389; found, 224.169779.

The identical procedure for **3a** provided **2a** in 95% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 1.00 (m, 1H), 1.2-1.8 (m, 19H), 1.89 (m, 1H), 2.14 (m, 2H), 2.45 (m, 2H). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 12.34. HRMS-EI (m/z): $[M]^+$ calcd for $C_{14}H_{25}P$, 224.169389; found, 224.169561.

Preparation of 4a and 4b. The appropriate phosphine, eg. **2b** (0.0249 g, 0.100 mmol), and 1 mL of THF were added to a 20 mL vial containing a stir bar. A solution of naphthylmethyl bromide (0.0298 g, 0.130 mmol) in THF (1 mL) was added to the vial and a solid immediately precipitated. The mixture was stirred for an additional hour after which time the vial was removed from the inert atmosphere box. The solid was collected by filtration and rinsed with pentane to give 0.0485 g of **4b** (98%) as a white solid. Ether was allowed to diffuse into a solution of the phosphonium salt in a minimal amount of methylene chloride to give crystals suitable for X-ray analysis. ^{1}H NMR (400 MHz, C_6D_6): δ 1.33 (m, 1H), 1.52 (m, 2H), 1.6-2.2 (m, 19H), 2.85 (m, 1H), 3.17 (m, 2H), 3.96 (d, J = 14 Hz, 2H), 7.57 (m, 3H), 7.93 (m, 2H), 7.97 (m, 2H). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 60.10. CCDC no. 291473.

The idential procedure for **2a** provided 0.0470 g of **4a** (95%). Diffusion of ether into a MeOH/acetonitrile solution of the phosphonium salt provided crystals suitable for X-ray analysis. ^{1}H NMR (400 MHz, C_6D_6): δ 0.97 (m, 1H), 1.16 (m, 4H), 1.60 (m, 1H), 1.68 (m, 2H), 1.79 (m, 2H), 1.92 (m, 4H), 2.0-2.2 (m, 7H), 2.40 (m, 2H), 3.27 (m, 2H), 4.30 (d, *J* = 14 Hz, 2H), 7.52 (d, *J* = 9 Hz, 1H), 7.59 (m, 2H), 7.95 (m, 3 H), 8.01 (d, *J* = 8 Hz, 1H). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 57.94. CCDC no. 291472.

General Procedure for Optimization Screens (Microwave protocol). To a 2 mL glass vial was added $[RhCl(coe)_2]_2$ (0.0036 g, 0.0050 mmol), **2a/b** (0.0069 g, 0.030 mmol), hexamethylbenzene (0.0020 g, 0.012 mmol), and DCB (0.4 mL). This solution was allowed to stand until the solids dissolved and a color change from orange to purple was noted (ca. 1-2 min). The appropriate heterocycle (0.100 mmol) and DCB (0.4 mL) were added to a glass microwave vial with a stir bar. The catalyst solution, the appropriate aryl halide (0.20 mmol) and base (0.30 mmol), were then added to the reaction vessel. The vial was sealed and heated for 40 min at 250 ºC. The reaction mixture was then diluted with 5 mL of ethyl acetate, 5 mL of methanol, and 1 mL of Et_3N, and analyzed by GC.

2-Phenylbenzimidazole: Typical Procedure for Cross-Coupling Azoles and Aryl Bromides (Microwave protocol). To a 5 mL glass microwave vial was added the appropriate heterocycle, e.g. benzimidazole (0.106 g, 0.897 mmol), a magnetic stir bar, and 2 mL of DCB. The catalyst solution (1.0 mL of a DCB (3.1 mL) solution of $[RhCl(coe)_2]_2$ (0.0997 g, 0.139 mmol) and **2a/b** (0.188 g, 0.837 mmol)) was then added. The appropriate aryl bromide, e.g. bromobenzene (0.20 mL, 1.8 mmol) and *i*-Pr_2*i*-BuN (0.55 mL, 2.7 mmol) were then added to the reaction vessel. The vial was sealed and heated for 40 min at 250 ºC. The reaction mixture was then cooled, quenched with excess Et_3N (1 mL), and concentrated under reduced pressure to remove the DCB. The residue was dissolved in a minimal amount of methanol and loaded onto a silica gel samplet (Biotage No. SAM-1107-16016) and purified using flash chromatography. A suitable gradient was calculated by the Biotage SP given a product R_f of 0.3 in 30% ethyl acetate/hexanes. The desired product was obtained as 0.139 g (80% yield, Table 2, entry 7) of a

white solid. In some cases, the concentration of the reactants was reduced. The amount of heterocycle (mmol) and the concentration (M) of the reaction is therefore provided for each entry.

General Procedure for Cross-Coupling Benzimidazole and Aryl Iodides (Conventional heating protocol). To a 25 mL sealable glass tube was added benzimidazole (0.059 g, 0.50 mmol), a magnetic stir bar, and 4 mL of DCB. The catalyst solution (1.0 mL of a THF (4.1 mL) solution of $[RhCl(coe)_2]_2$ (0.0734 g, 0.102 mmol) and **2a/b** (0.1378 g, 0.6152 mmol)) was then added. The appropriate aryl halide (1.0 mmol) and *i*-Pr_2*i*-BuN (0.31 mL, 1.5 mmol) were then added to the reaction vessel. The vial was sealed and heated for 24 h at 150 ºC. The reaction mixture was cooled, quenched with excess Et_3N (1 mL), and concentrated under reduced pressure to remove the THF. The residue was dissolved in a minimal amount of methanol and loaded onto a silica gel samplet (Biotage No. SAM-1107-16016) and purified using flash chromatography. A suitable gradient was calculated by the Biotage SP given a product R_f of 0.3 in ethyl acetate/hexanes.

General Procedure for Cross-coupling Benzimidazole and Aryl Bromides (Conventional heating protocol in NMR tube). To a glass vial was added $[RhCl(coe)_2]_2$ (0.0062 g, 0.0086 mmol), **2a/b** (0.0122 g, 0.0545 mmol), and d_8-THF (0.68 mL). This solution was allowed to stand until the solids dissolved and a color change from orange to purple was noted. Similarly, benzimidazole (0.0211 g, 0.179 mmol), 2,6-dimethoxytoluene (0.0080 g, 0.053 mmol), and d_8-THF (0.68 mL) were added to a second vial. Aliquots of these solutions (0.15 mL) were then added to an oven-dried, medium-walled NMR tube. The appropriate aryl bromide (0.08 mmol) and *i*-Pr_2*i*-BuN (0.025 mL, 0.12 mmol) were then added to the NMR tube using additional d_8-THF (0.1 mL) to ensure quantitative transfer of the reagents. The tube was fitted with a Cajon adapter, removed from the inert atmosphere box, attached to a vacuum line, and flame sealed. The tube was heated at 150 °C and the reaction monitored by NMR spectroscopy.

2-Phenylbenzimidazole (5): The product was synthesized using the typical procedure for cross-coupling azoles and aryl halides using microwave radiation with iodo- and bromobenzene, the general procedure for cross-coupling benzimidazole and aryl iodides using conventional heating, and the general procedure for cross-coupling benzimidazole and aryl bromides using conventional heating. Both

microwave reactions were conducted at 0.9 mmol scale and a concentration of 0.3 M. Compound **5** was isolated as an off-white solid following silica gel chromatography as described in the typical procedure for cross-coupling azoles and aryl halides. Microwave heating using iodobenzene: 0.159 g (91%); Microwave heating using bromobenzene: 0.139 g (80%); Conventional heating using iodobenzene: 0.0738 g (76%). mp 289-291 °C (lit. 285-286 °C).[10] ^{1}H NMR (d_6-DMSO, 400 MHz): δ 8.05 (dd, J = 8.2, 1.6 Hz, 2H), 7.56 (s, 1H), 7.49 (m, 5H), 7.21 (m, 2H).

2-(4-Trifluoromethylphenyl)-benzimidazole (6): The product was synthesized using the typical procedure for cross-coupling azoles and aryl halides using microwave radiation with iodo- and bromobenzene, the general procedure for cross-coupling benzimidazole and aryl iodides using conventional heating, and the general procedure for cross-coupling benzimidazole and aryl bromides using conventional heating. Both microwave reactions were conducted at 0.9 mmol scale and a concentration of 0.3 M. Compound **6** was isolated as an off-white solid following flash chromatography eluting with 10-80% EtOAc/hexanes. Microwave heating using *p*-iodobenzotrifluoride: 0.138 g (58%); Microwave heating using *p*-bromobenzotrifluoride: 0.188 g (77%); Conventional heating using *p*-iodobenzotrifluoride: 0.0905 g (68%). mp 264-266 °C. ^{1}H NMR (CD_3OD, 400 MHz): δ 8.27 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 7.8 Hz, 2H), 7.65 (m, 2H), 7.31 (m, 2H). The N-H proton was not observed. ^{13}C NMR (CD_3OD, 100 MHz): δ 150.14, 133.28, 131.32, 130.99, 126.92, 125.71, 125.39, 122.98 (broad). ^{19}F NMR (CD_3OD, 376 MHz): δ −63.16. (HRMS-EI (m/z): $[M]^+$ calcd for $C_{14}H_9N_2F_3$, 262.071783; found, 262.071845.

2-(4-Methoxyphenyl)-benzimidazole (7): The product was synthesized using the typical procedure for cross-coupling azoles and aryl halides using microwave radiation with bromobenzene, the general procedure for cross-coupling benzimidazole and aryl iodides using conventional heating, and the general procedure for cross-coupling benzimidazole and aryl bromides using conventional heating. The microwave reaction was conducted at 0.4 mmol scale and a concentration of 0.1 M. Compound **7** was isolated as an off-white solid following flash chromatography eluting with 10-80% EtOAc/hexanes. Microwave heating using *p*-bromoanisole: 0.0488 g (54%); Conventional heating using *p*-iodoanisole:

0.111 g (99%). mp 229-230 °C (lit. 222-225 °C).[8] ^{1}H NMR (CD_3OD, 400 MHz): δ 8.27 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.65 (m, 2H), 7.31 (m, 2H). The N-H proton was not observed.

2-(4-Cyanophenyl)-benzimidazole (8): The product was synthesized using the typical procedure for cross-coupling with microwave radiation. The reaction was conducted at 0.1 M. The crude reaction mixture was purified by flash chromatography eluting with 30% EtOAc/hexanes to provide 0.0792 g, 90% yield (0.4 mmol scale) of **8** as an off-white solid. mp 261-262 °C (lit. 261-262 °C).[8] ^{1}H NMR (d_6-DMSO, 400 MHz): δ 13.19 (s, 1H), 8.35 (d, *J* = 8.1 Hz, 2H), 8.03 (d, *J* = 7.8 Hz, 2H), 7.65 (m, 2H), 7.26 (m, 2H).

2-(4-Chlorophenyl)-benzimidazole (9): The product was synthesized using the typical procedure for cross-coupling with microwave radiation. The reaction was conducted at 0.1 M. The crude reaction mixture was purified by flash chromatography eluting with 30% EtOAc/hexanes to provide 0.0462 g, 67% yield (0.3 mmol scale) of **9** as an off-white solid. mp 288-290 °C (lit. 290-292 °C).[8] ^{1}H NMR (d_6-DMSO, 400 MHz): δ 8.09 (d, *J* = 8.6 Hz, 2H), 7.65 (b s, 2H), 7.65 (m, 2H), 7.26 (m, 2H).

2-(4-Propionylphenyl)-benzimidazole (10): The product was synthesized using the typical procedure for cross-coupling with microwave radiation. Two identical reactions were conducted at 0.05 M and combined due to volume constraints of the microwave reaction vials. The crude reaction mixture was purified by flash chromatography eluting with 30% EtOAc/hexanes to provide 0.0750 g, 75% yield (2 x 0.2 mmol scale) of **10** as an off-white solid. mp 212-213 °C. ^{1}H NMR (CD_3OD, 400 MHz): δ 9.61 (s, 1H), 8.16 (d, *J* = 8.6 Hz, 2H), 8.11 (d, *J* = 8.6 Hz, 2H), 7.87 (m, 1H), 7.53 (m, 1H), 7.33 (m, 2H), 3.07 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (CD_3OD, 100 MHz): δ 200.66, 150.66, 137.63, 133.52, 128.37, 126.47, 123.02 (broad), 122.89 (broad), 31.39, 7.04. HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{14}N_2O$, 250.110550; found, 250.110613.

2-(4-Carboxamidophenyl)-benzimidazole (11): The product was synthesized using the typical procedure for cross-coupling with microwave radiation. The reaction was conducted at 0.1 M. The crude reaction mixture was purified by flash chromatography eluting with EtOAc to provide 0.0593 g, 60% (0.4 mmol scale) of **11** as a white solid. mp 336-337 °C. ^{1}H NMR (d_6-DMSO, 400 MHz): δ 13.05 (b s, 1H),

8.25 (d, *J* = 8.1 Hz, 1H), 8.10 (s, 1H), 8.04 (d, *J* = 8.1 Hz, 2H), 7.62 (m, 2H), 7.50 (b s, 1H), 7.24 (m, 2H). ^{13}C NMR (d_6-DMSO, 100 MHz): δ 167.80, 150.93, 135.58, 133.01, 128.61, 126.65, 123.40, 122.38, 111.96. HRMS-EI (m/z): $[M]^+$ calcd for $C_{14}H_{11}N_3O$, 237.090212; found, 237.090978.

2-(4-Biphenyl)-benzimidazole (12): The product was synthesized using the typical procedure for cross-coupling with microwave radiation. The reaction was conducted at 0.3 M. The crude reaction mixture was purified by flash chromatography eluting with 30% EtOAc/hexanes to provide 0.132 g, 81% yield (0.6 mmol scale) of **12** as a white solid. mp 300-301 °C (lit. 294-296 °C).[8] ^{1}H NMR (d_6-DMSO, 400 MHz): δ 12.99 (b s, 1H), 8.29 (d, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.62 (m, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.22 (m, 2H).

2-(4-Methylphenyl)-benzimidazole (13): The product was synthesized using the typical procedure for cross-coupling with microwave radiation. The reaction was conducted at 0.3 M. The crude reaction mixture was purified by flash chromatography eluting with 30% EtOAc/hexanes to provide 0.114 g, 91% yield (0.6 mmol scale) of **13** as a white solid. mp 272-276 °C (lit. 270-272 °C).[8] ^{1}H NMR (d_6-DMSO, 400 MHz): δ 12.84 (b s, 1H), 8.08 (d, *J* = 7.8 Hz, 2H), 7.53 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.19 (m, 2H), 2.38 (s, 3H).

2-(3-Carboethoxyphenyl)-benzimidazole (14): The product was synthesized using the typical procedure for cross-coupling with microwave radiation. Two identical reactions were conducted at 0.05 M and combined due to volume constraints of the microwave reaction vials. The crude reaction mixture was purified by flash chromatography eluting with 30% EtOAc/hexanes to provide 0.0752 g, 70% yield (2 x 0.2 mmol scale) of **14** as an off-white solid. mp 155-158 °C. ^{1}H NMR (CD_3OD, 400 MHz): δ 9.59 (s, 1H), 8.62 (t, *J* = 1.5 Hz, 1H), 8.37 (d,t, *J* = 8.0, 1.2 Hz, 1H), 8.17 (d,t, *J* = 7.8, 1.5 Hz, 1H), 7.86 (m, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.52 (m, 1H), 7.32 (m, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (CD_3OD, 100 MHz): δ 165.87, 150.83, 131.36, 130.60, 130.54, 130.14, 120.07, 128.74, 127.26, 126.40, 122.76, 61.07, 13.21. HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{14}N_2O_2$, 266.105315; found, 266.105528.

2-(3-Methylphenyl)-benzimidazole (15): The product was synthesized using the typical procedure for cross-coupling with microwave radiation. The reaction was conducted at 0.1 M. The crude reaction mixture was purified by flash chromatography eluting with 20% EtOAc/hexanes to provide 0.067 g, 79% yield (0.4 mmol scale) of **15** as an off-white solid. mp 220-221 °C (lit. 217-219 °C).[11] ^{1}H NMR (d_6-DMSO, 400 MHz): δ 12.88 (s, 1H), 8.03 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 6.8 Hz, 1H), 7.54 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.21 (m, 2H).

2-(3-Ethoxyphenyl)-benzimidazole (16): The product was synthesized using the typical procedure for cross-coupling with microwave radiation. The reaction was conducted at 0.05 M. The crude reaction mixture was purified by flash chromatography eluting with 7-60% EtOAc/hexanes to provide 0.0374 g of a mixture of **15** and **5** as an off-white solid. This material was further purified by reverse phase chromatography eluting with 5-95% acetonitrile/water to provide 0.0217 g, 46% yield (0.2 mmol scale) of **15** as a white solid. mp 209-212. ^{1}H NMR (CD_3OD, 400 MHz): δ 7.65 (m, 4H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.27 (m, 2H), 7.05 (2, *J* = 8.1 Hz, 1H), 4.15 (q, *J* = 6.8 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H). ^{13}C NMR (CD_3OD, 100 MHz): δ 159.60, 151.92, 130.78, 129.81, 122.55 (broad), 118.51, 116.50, 112.05, 63.31, 13.74. HRMS-EI (m/z): $[M]^+$ calcd for $C_{15}H_{14}N_2O$, 238.110613; found, 238.110639.

1-Methyl-2-phenylbenzimidazole (17): The product was synthesized using the typical procedure for cross-coupling with microwave radiation. The reaction was conducted at 0.1 M. The crude reaction mixture was purified by flash chromatography eluting with 10% EtOAc/hexanes to provide 0.0460 g, 55% yield (0.4 mmol scale) of **17** as an off-white solid. mp 92-94 °C (lit. 94-96 °C).[1] ^{1}H NMR (d_6-DMSO, 400 MHz): δ 7.85 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.60 (m, 3H), 7.27 (m, 2H), 3.90 (s, 3H).

2-Phenylbenzoxazole (18): The product was synthesized using the typical procedure for cross-coupling with microwave radiation. The reaction was conducted at 0.1 M. The crude reaction mixture was purified by flash chromatography eluting with 5% EtOAc/hexanes to provide 0.0485 g, 63% (0.4 mmol scale) of **18** as a white solid. mp 100-102 °C (lit. 102-103 °C).[1] ^{1}H NMR (d_6-DMSO, 400 MHz): δ 8.20 (dd, *J* = 7.4, 1.6 Hz, 2H), 7.80 (td, *J* = 6.6, 2.4 Hz, 2H), 7.60 (m, 3H), 7.40 (m, 2H).

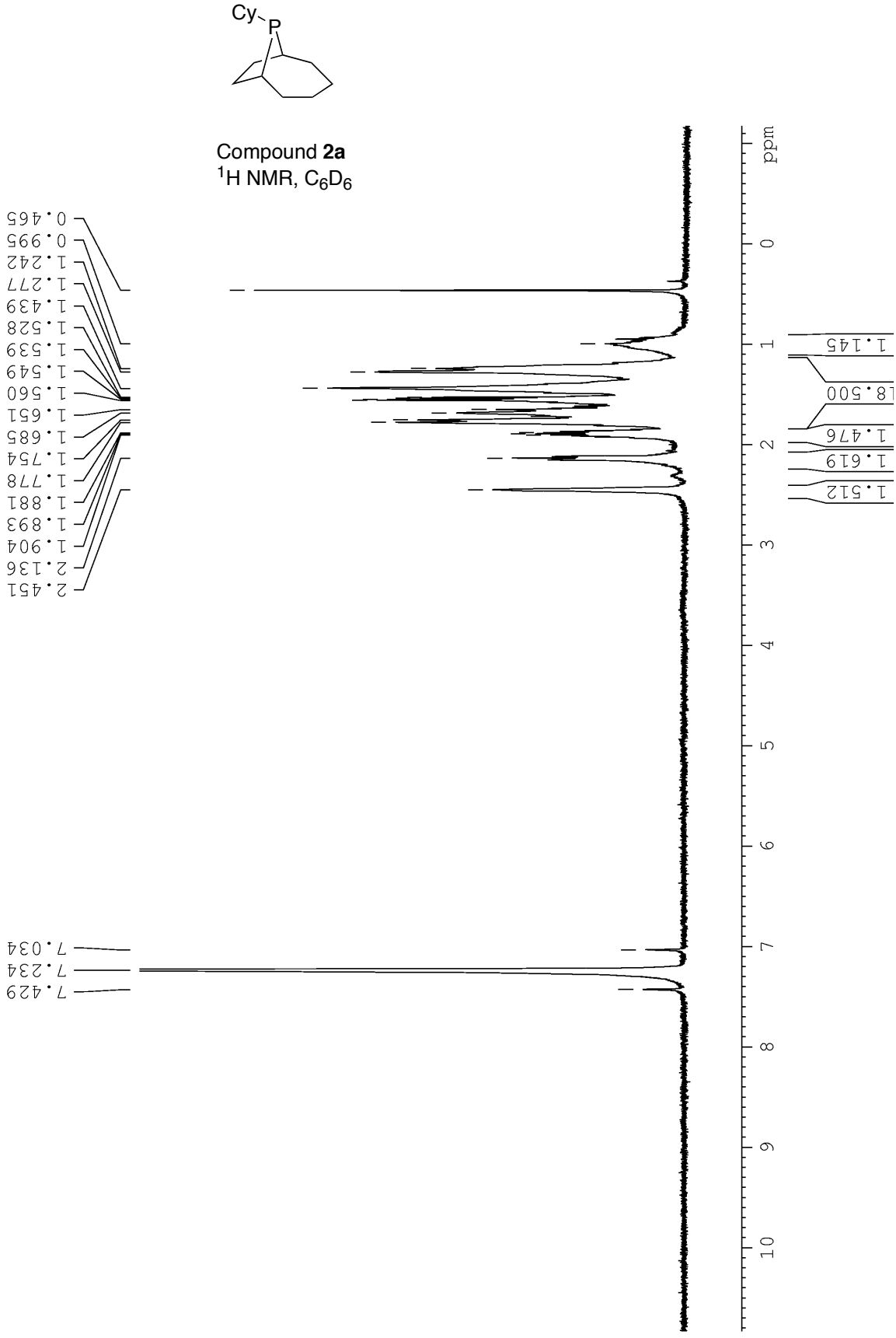
3,5-Diphenyl-4*H*-[1,2,4]triazole (19): The product was synthesized using the typical procedure for cross-coupling with microwave radiation. The reaction was conducted at 0.05 M. The crude reaction mixture was purified by flash chromatography eluting with 20% EtOAc/hexanes to provide 0.0199 g, 45% yield (0.2 mmol scale) of **19** as an off-white solid. mp 189-192 °C (lit. 192.7-193.3 °C).[12] ^{1}H NMR (d_6-DMSO, 400 MHz): δ 14.50 (s, 1H), 7.97 (d, *J* = 6.8 Hz, 4H), 7.49 (b s, 6H).

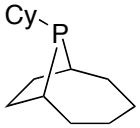
2,5-Diphenyl-4-(4-methoxyphenyl)-imidazole (21): The product was synthesized using the typical procedure for cross-coupling with microwave radiation. The reaction was conducted at 0.05 M. The crude reaction mixture was purified by flash chromatography eluting with 5-20% EtOAc/hexanes to provide 0.0487 g, 75% yield (0.2 mmol scale) of **21** as an off-white solid. mp 226-227 °C (lit. 225-226 °C).[13] ^{1}H NMR (CD_3OD, 400 MHz): δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.46 (m, 4H), 7.39, (m, 3H), 7.32 (t, *J* = 7.1 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H)

2,5-Diphenyl-4-(4-fluorophenyl)-imidazole (22): The product was synthesized using the typical procedure for cross-coupling with microwave radiation. The reaction was conducted at 0.1 M. The crude reaction mixture was purified by flash chromatography eluting with 5-40% EtOAc/hexanes to provide 0.1083 g, 86% yield (0.4 mmol scale) of **22** as an off-white solid. mp 257-258 °C (lit. 256-257 °C).[11] ^{1}H NMR (CD_3OD, 400 MHz): δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.47 (m, 6H), 7.36, (m, 4H), 7.07 (t, *J* = 8.2 Hz, 2H)

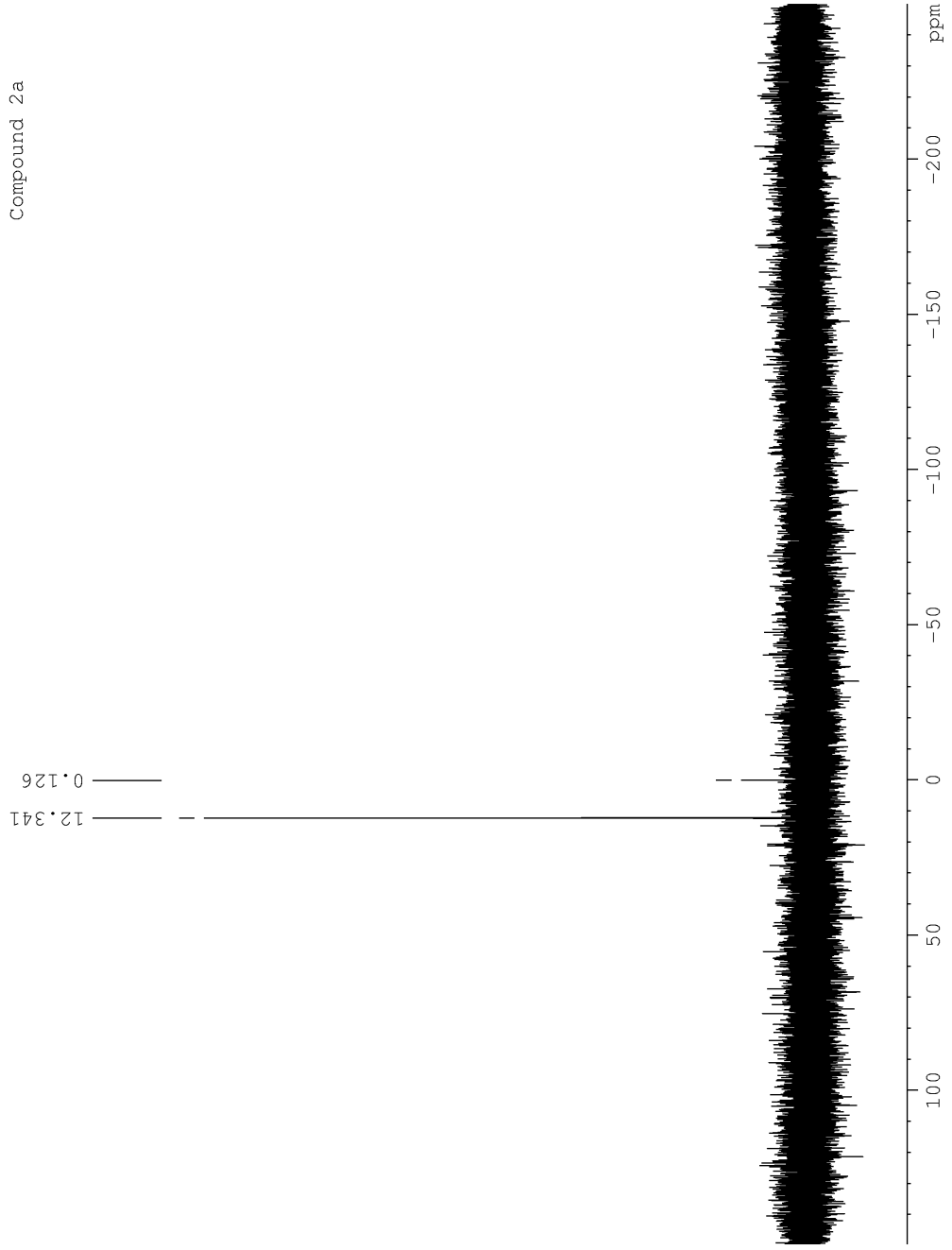
2-Phenylquinazoline (23): The product was synthesized using the typical procedure for cross-coupling with microwave radiation. The reaction was conducted at 0.1 M. The crude reaction mixture was purified by flash chromatography eluting with 5% EtOAc/hexanes to provide 0.0422 g, 50% yield (0.4 mmol scale) of **23** as a white solid. mp 100-102 °C (lit. 100-101 °C).[1] ^{1}H NMR (d_6-DMSO, 400 MHz): δ 8.62 (d, *J* = 6.4 Hz, 2H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 7.0 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 (m, 3H).

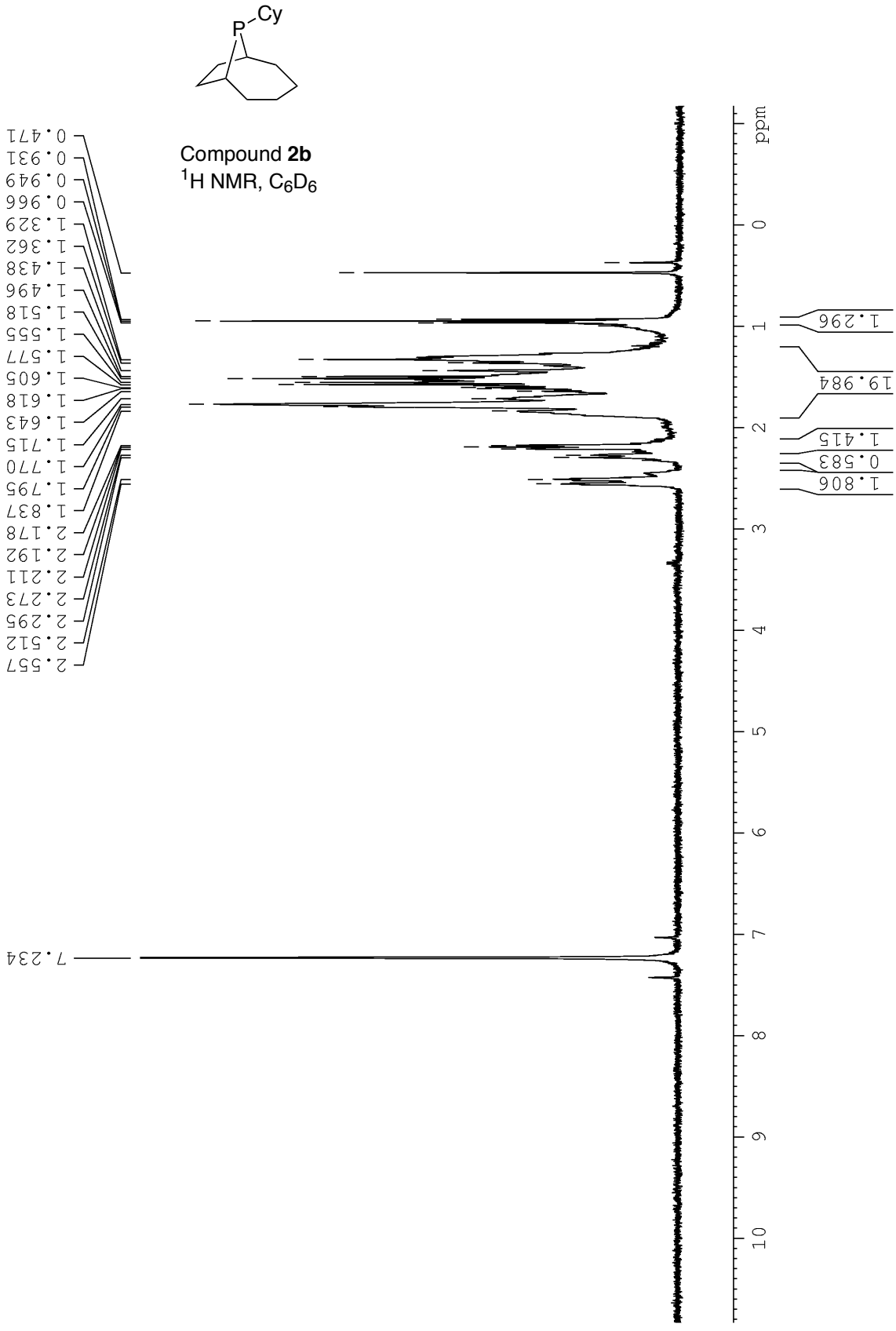
Spectra for New Comoupnds:

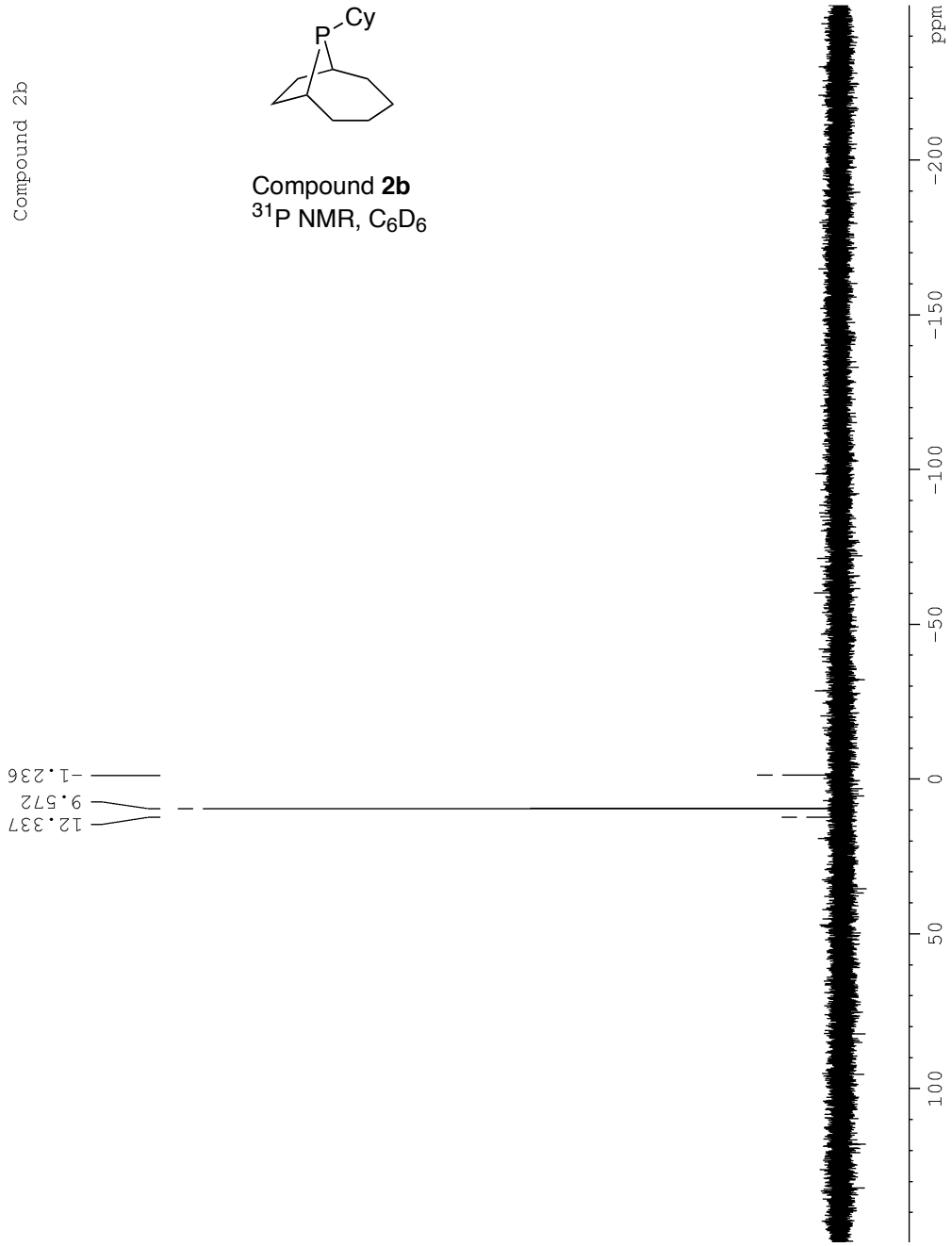


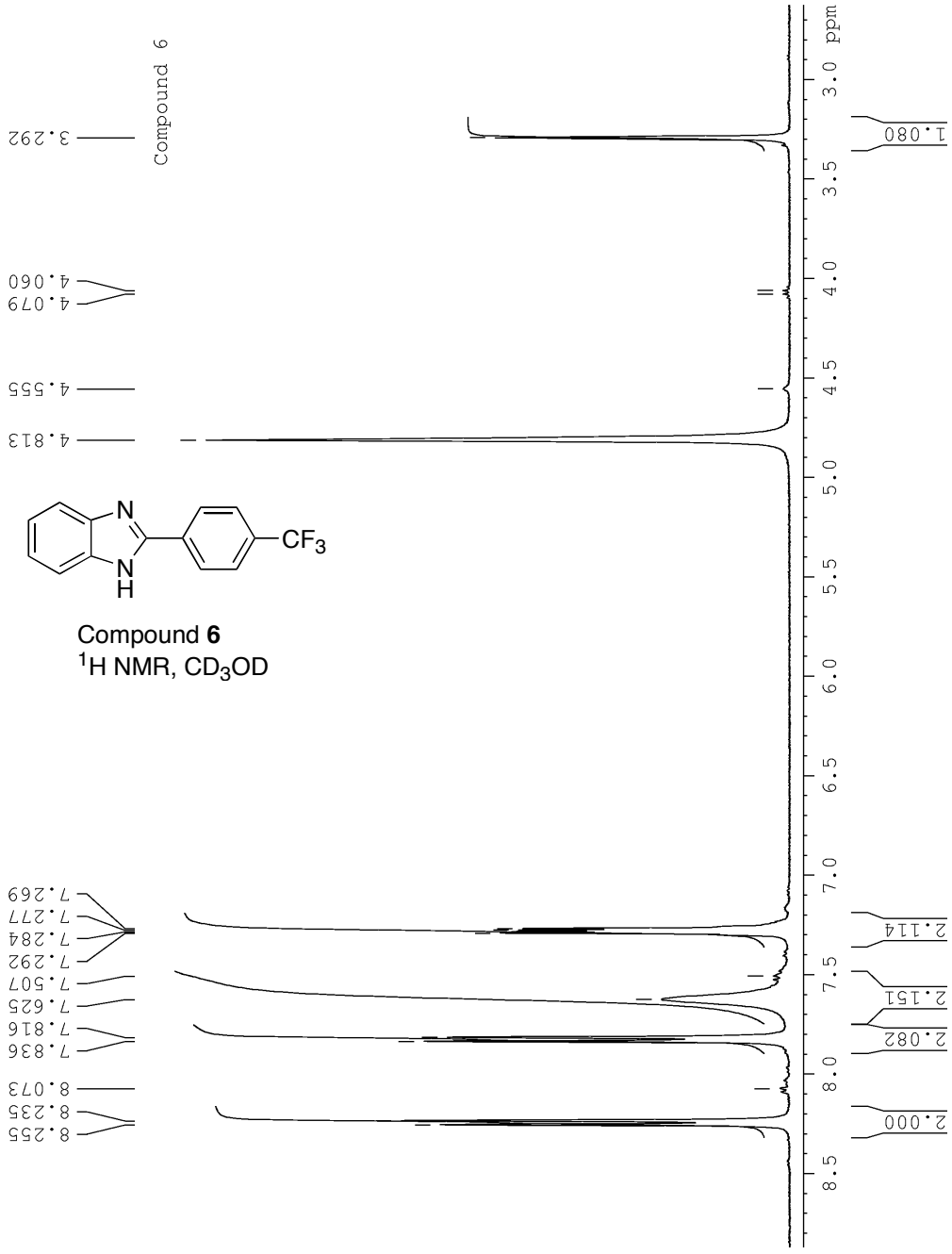


Compound **2a**
^{31}P NMR, C_6D_6

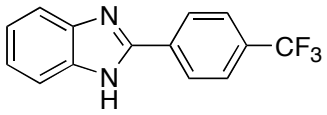



P
Cy
Compound **2b**
^{1}H NMR, C_6D_6
ppm
0.471
0.931
0.949
0.966
1.329
1.362
1.438
1.496
1.518
1.555
1.577
1.605
1.618
1.643
1.715
1.770
1.795
1.837
2.178
2.192
2.211
2.273
2.295
2.512
2.557
7.234
1.296
19.984
1.415
0.583
1.806

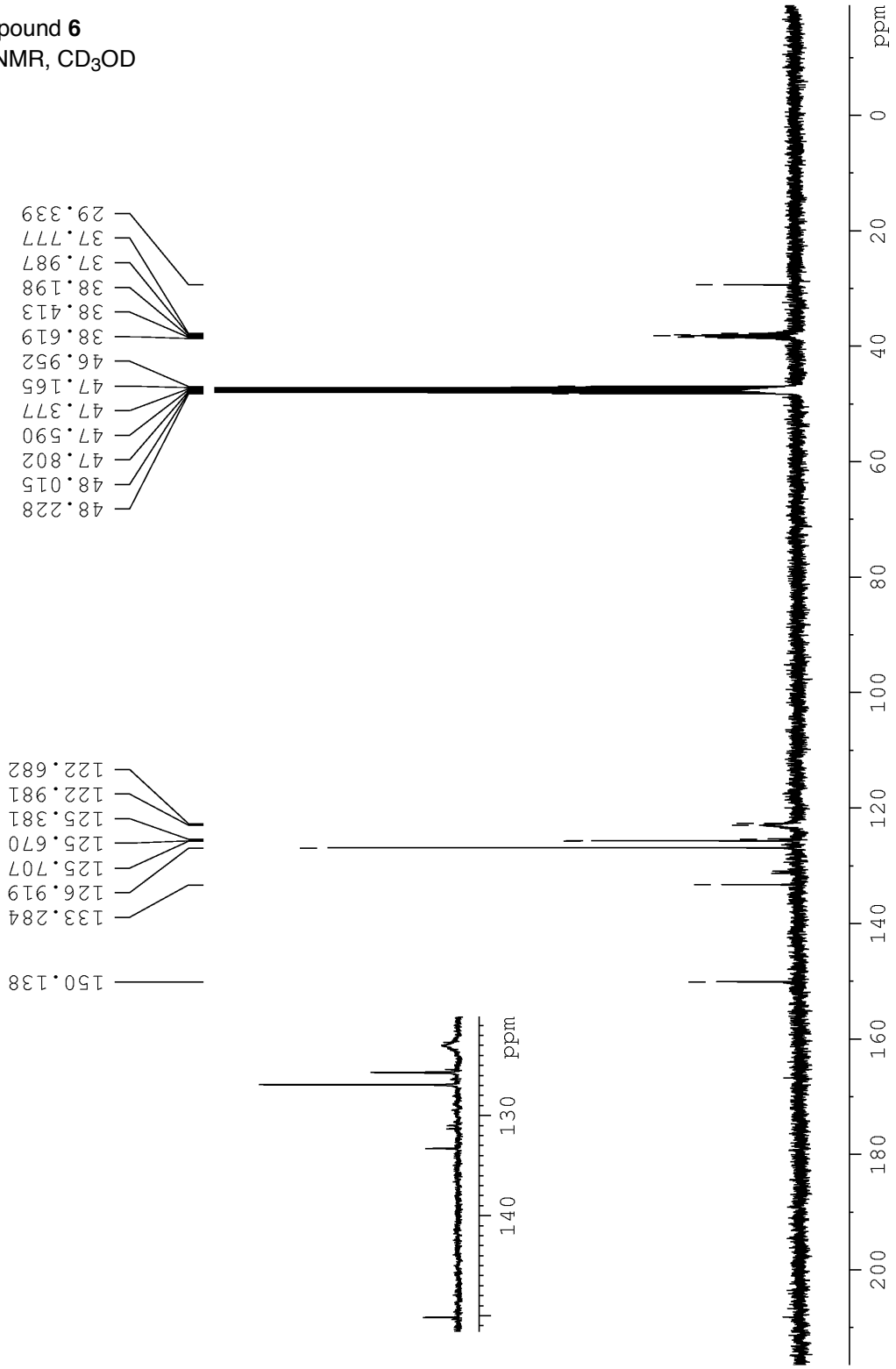

Compound 2b
P
Cy
Compound **2b**
^{31}P NMR, C_6D_6
12.337
9.572
-1.236
100
50
0
-50
-100
-150
-200
ppm

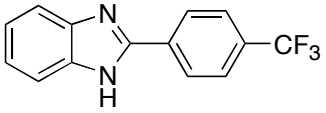


Compound **6**
^{1}H NMR, CD_3OD

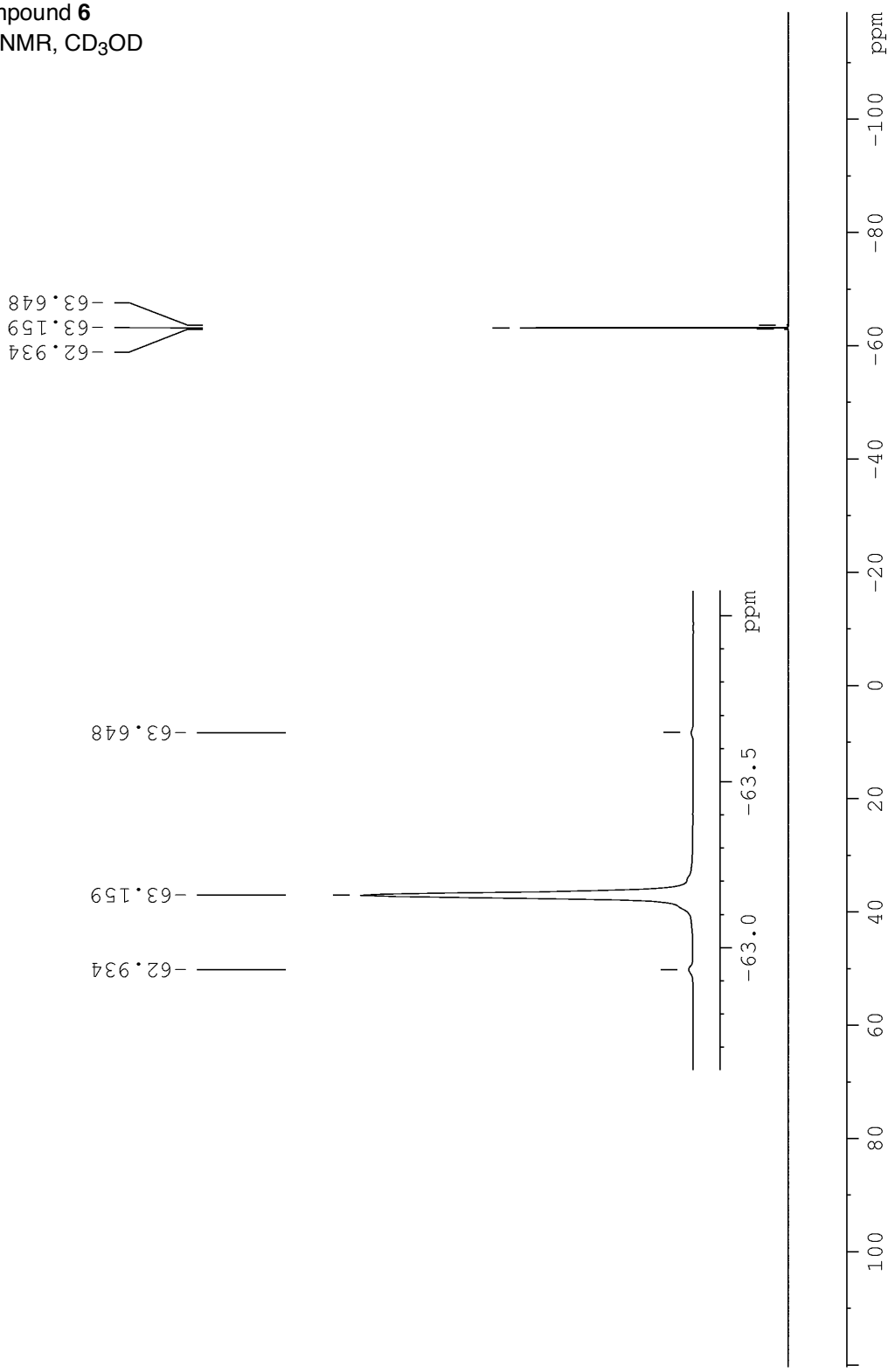


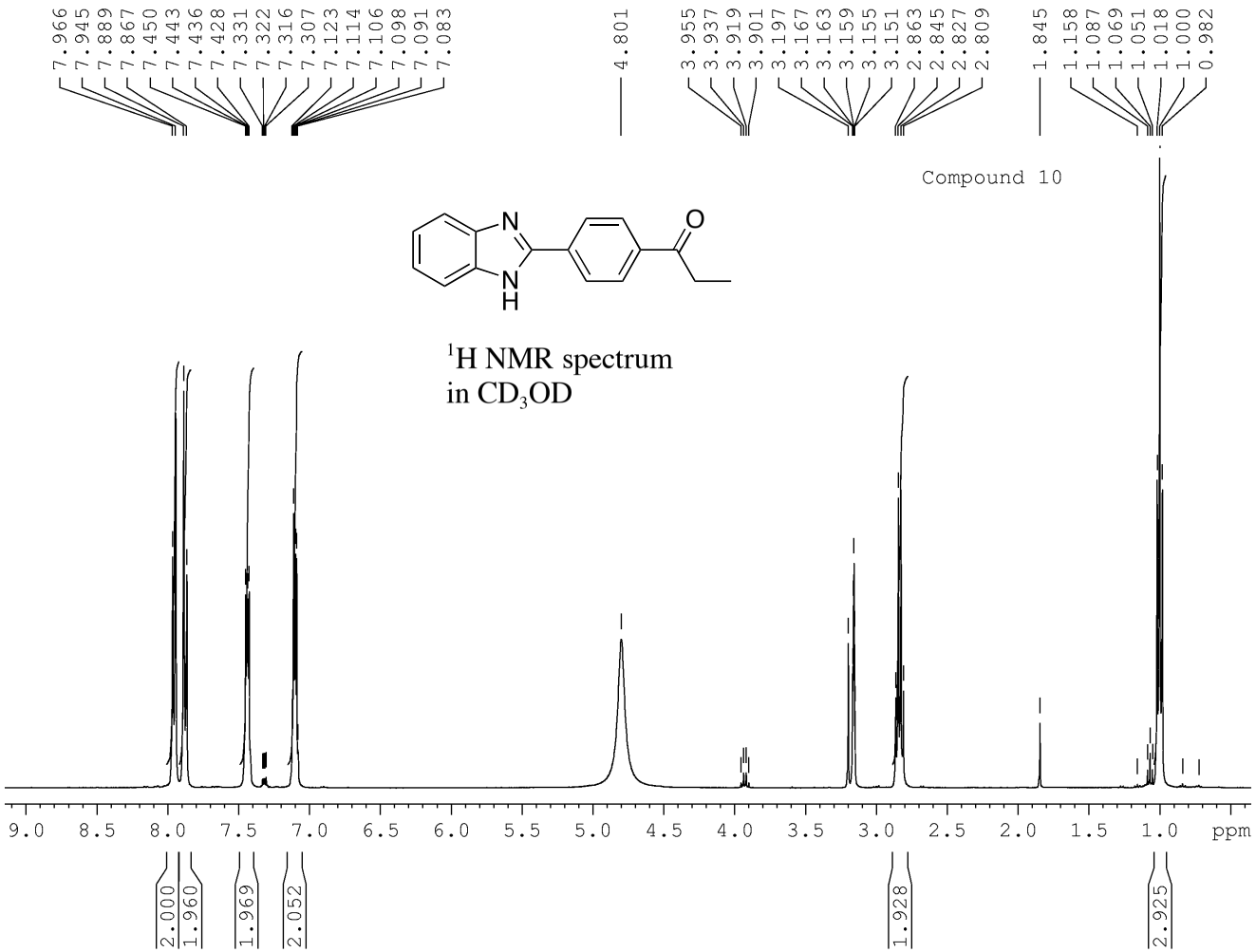
Compound **6**
^{13}C NMR, CD_3OD

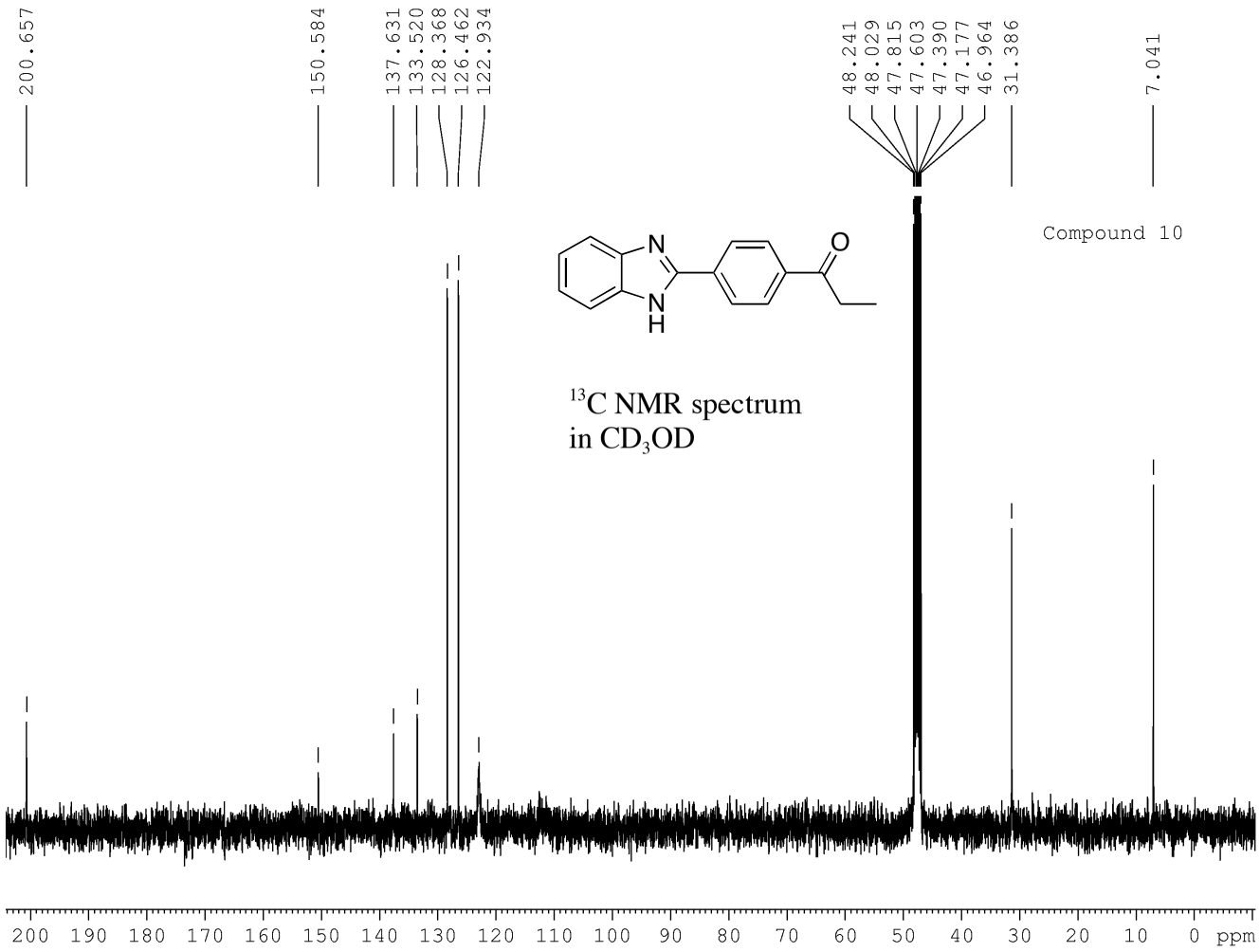


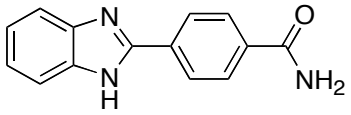


Compound **6**
^{19}F NMR, CD_3OD

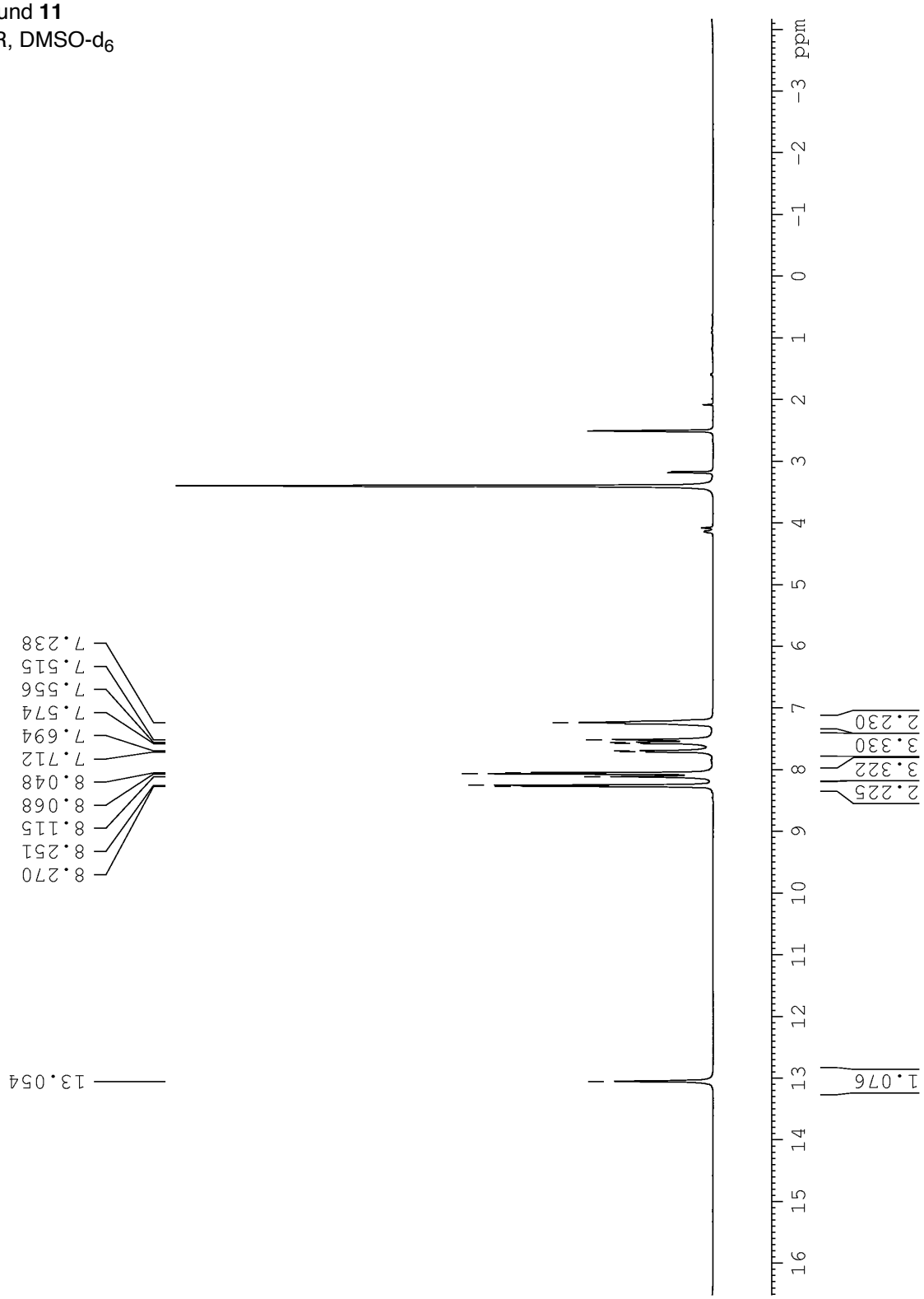


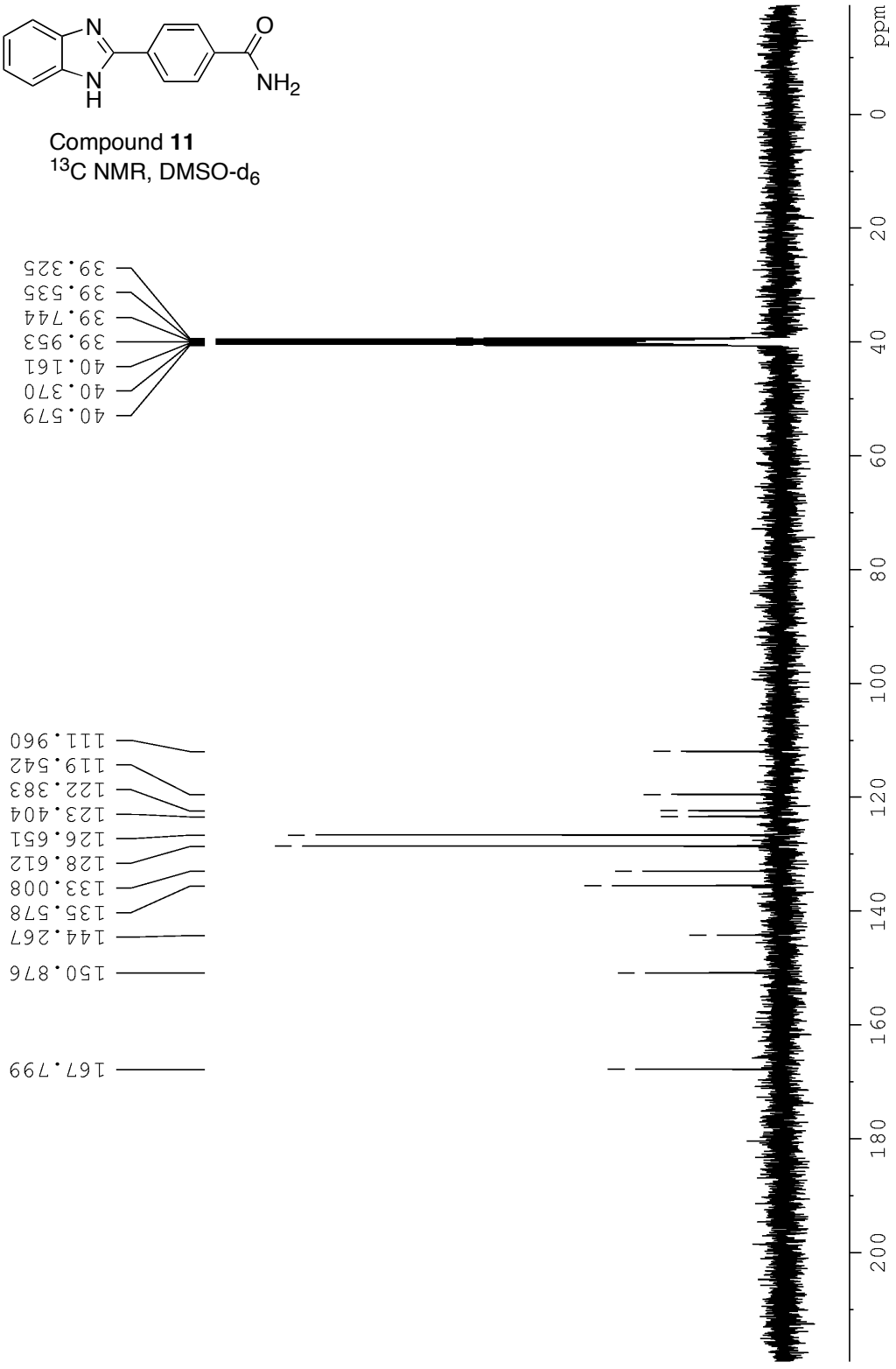

7.966
7.945
7.889
7.867
7.450
7.443
7.436
7.428
7.331
7.322
7.316
7.307
7.123
7.114
7.106
7.098
7.091
7.083
4.801
3.955
3.937
3.919
3.901
3.197
3.167
3.163
3.159
3.155
3.151
2.863
2.845
2.827
2.809
1.845
1.158
1.087
1.069
1.051
1.018
1.000
0.982
Compound 10
N
O
N
H
^{1}H NMR spectrum
in CD_3OD
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.000
1.960
1.969
2.052
1.928
2.925

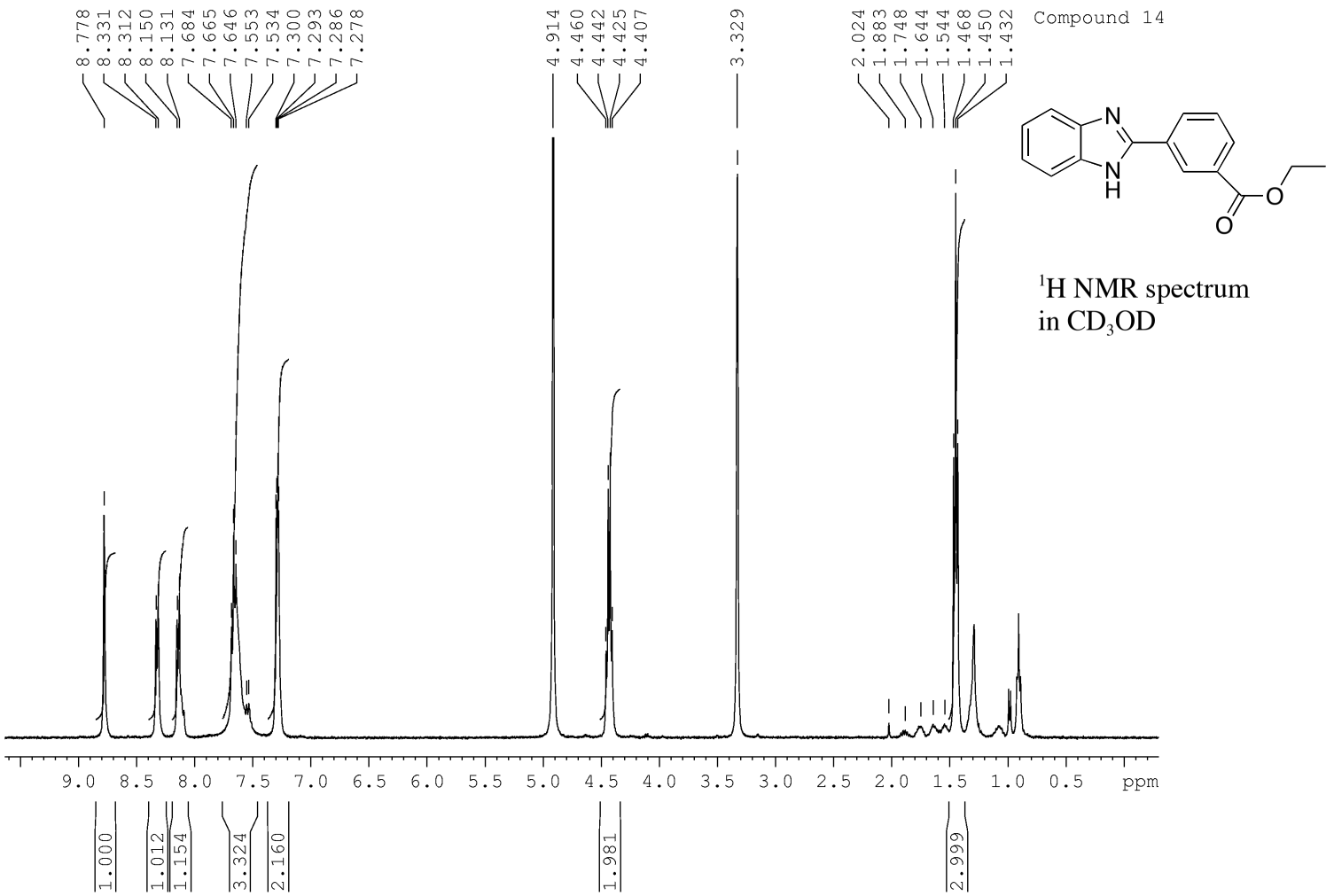

200.657
150.584
137.631
133.520
128.368
126.462
122.934
48.241
48.029
47.815
47.603
47.390
47.177
46.964
31.386
7.041
Compound 10
N
N
H
O
^{13}C NMR spectrum
in CD_3OD
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

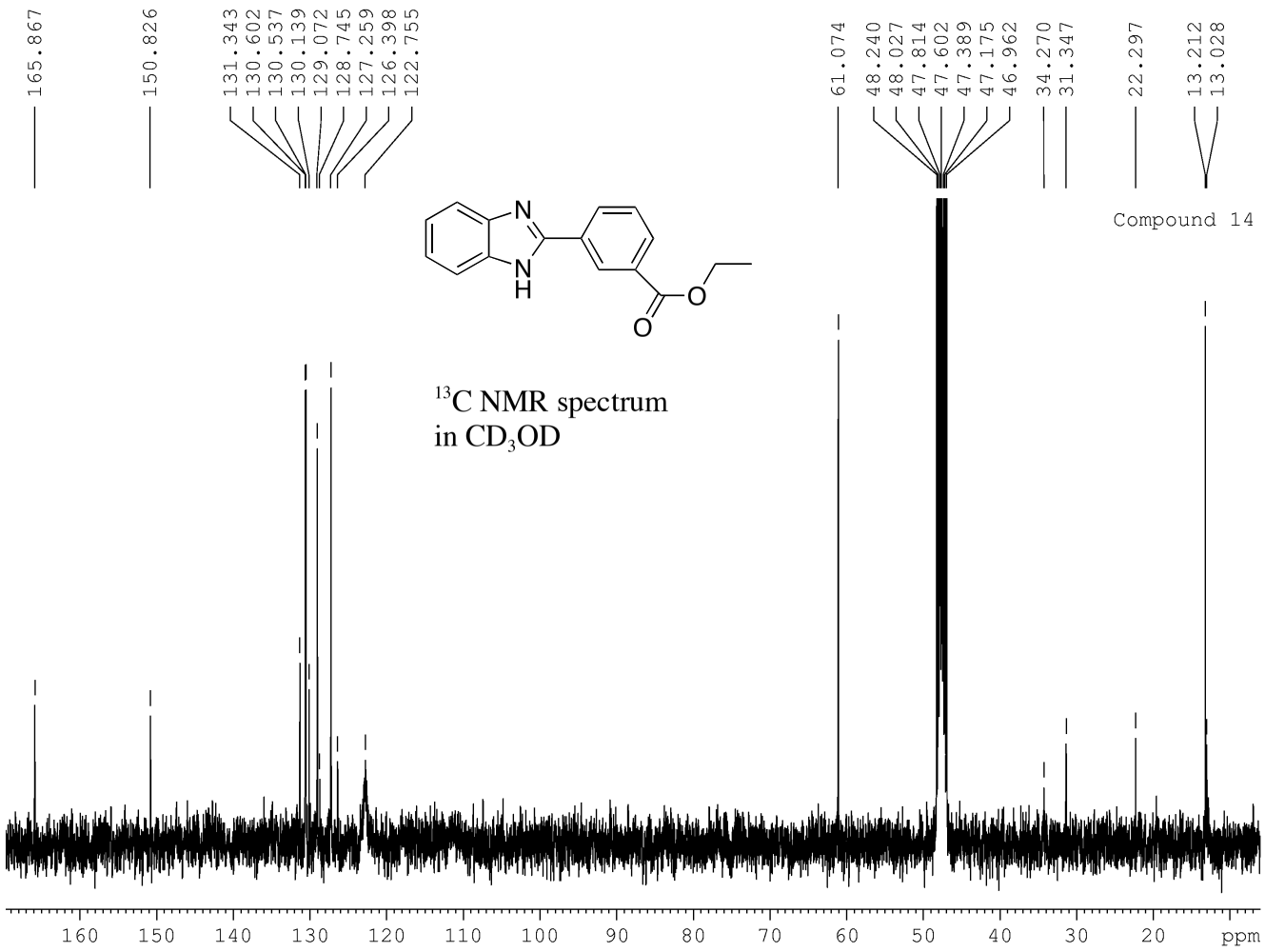


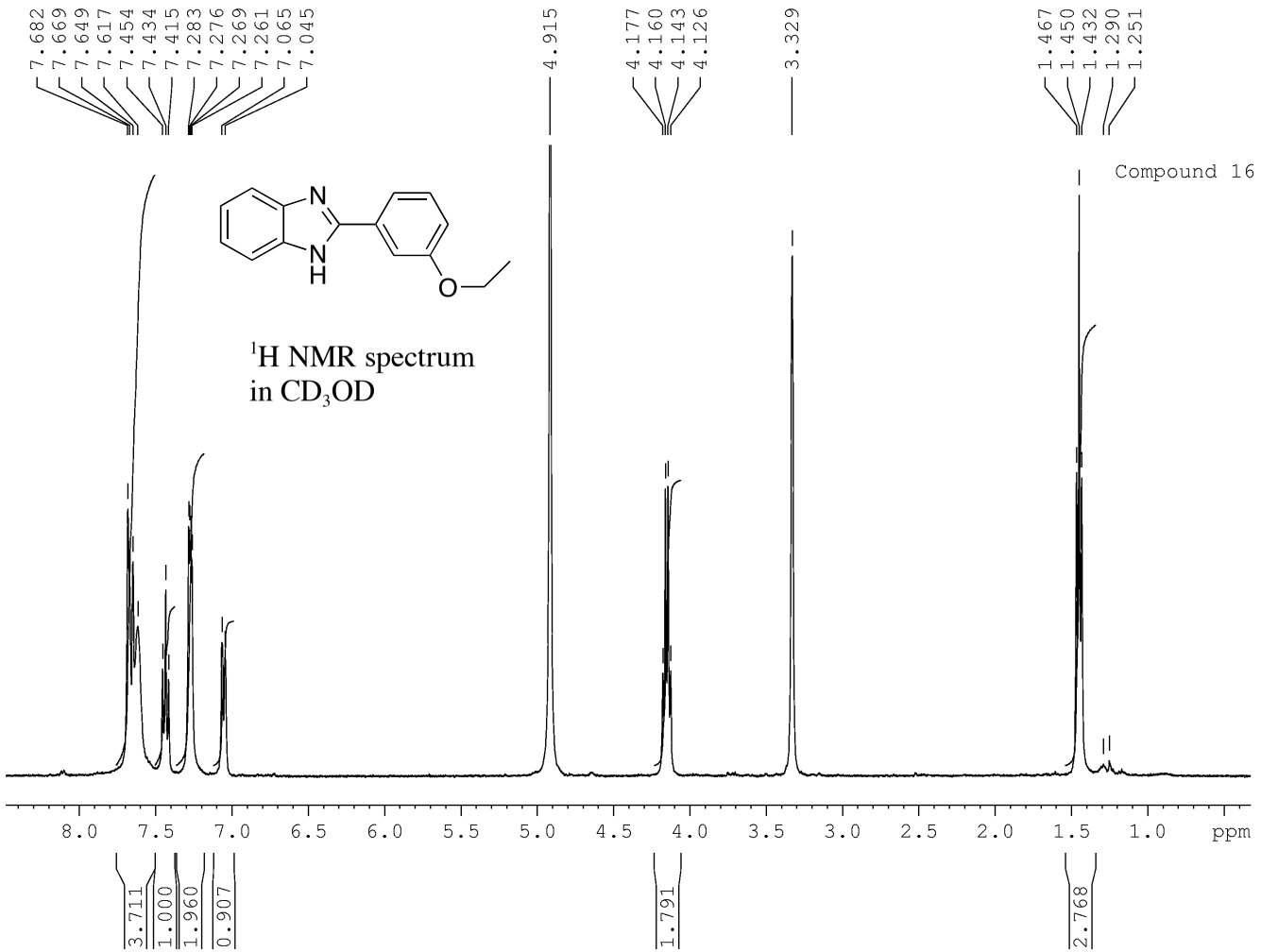
Compound **11**
^{1}H NMR, DMSO-d_6

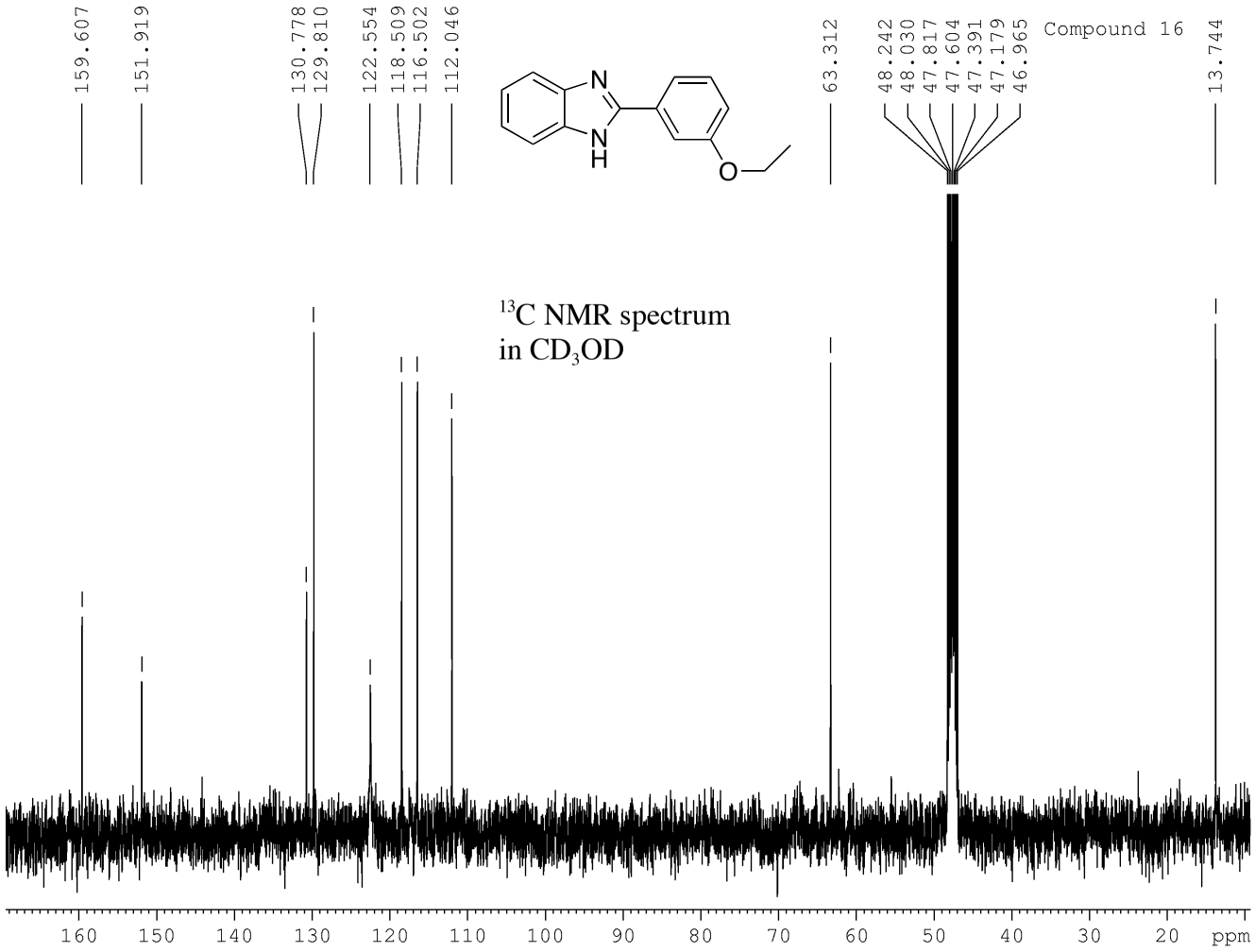



N
N
H
O
NH2
Compound 11
13C NMR, DMSO-d6
39.325
39.535
39.744
39.953
40.161
40.370
40.579
111.960
119.542
122.383
123.404
126.651
128.612
133.008
135.578
144.267
150.876
167.799
ppm
0
20
40
60
80
100
120
140
160
180
200


Compound 14
8.778
8.331
8.312
8.150
8.131
7.684
7.665
7.646
7.553
7.534
7.300
7.293
7.286
7.278
4.914
4.460
4.442
4.425
4.407
3.329
2.024
1.883
1.748
1.644
1.544
1.468
1.450
1.432
N
N
H
O
O
1H NMR spectrum
in CD3OD
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.012
1.154
3.324
2.160
1.981
2.999


165.867
150.826
131.343
130.602
130.537
130.139
129.072
128.745
127.259
126.398
122.755
61.074
48.240
48.027
47.814
47.602
47.389
47.175
46.962
34.270
31.347
22.297
13.212
13.028
Compound 14
N
N
H
O
O
13C NMR spectrum
in CD3OD
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.682
7.669
7.649
7.617
7.454
7.434
7.415
7.283
7.276
7.269
7.261
7.065
7.045
4.915
4.177
4.160
4.143
4.126
3.329
1.467
1.450
1.432
1.290
1.251
Compound 16
N
N
H
O
^{1}H NMR spectrum
in CD_3OD
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
3.711
1.000
1.960
0.907
1.791
2.768


159.607
151.919
130.778
129.810
122.554
118.509
116.502
112.046
63.312
48.242
48.030
47.817
47.604
47.391
47.179
46.965
13.744
Compound 16
N
N
H
O
^{13}C NMR spectrum
in CD_3OD
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

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[8] This procedure is essentially that obtained from a personal communication which since been submitted for publication: Catherine L. Dwyer, Megan M. Kirk, Wolfgang H. Meyer, Werner Janse van Rensburg, Grant S. Forman, Organometallics, submitted for publication.

[9] This procedure is essentially that used by Zhang and co-workers for purification of another bicicylic phosphine. Chen, Z.; Jiang, Q.; Zhu, G.; Xiao, D.; Cao, P.; Guo, C.; Zhang, X. *J. Org. Chem.* **1997**, *62*, 4521-4523.

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