Supporting Information

for

$PdCl_2$-Catalyzed Efficient Allylation and Benzylation of Heteroarenes under Ligand, Base/Acid, and Additive-Free Conditions

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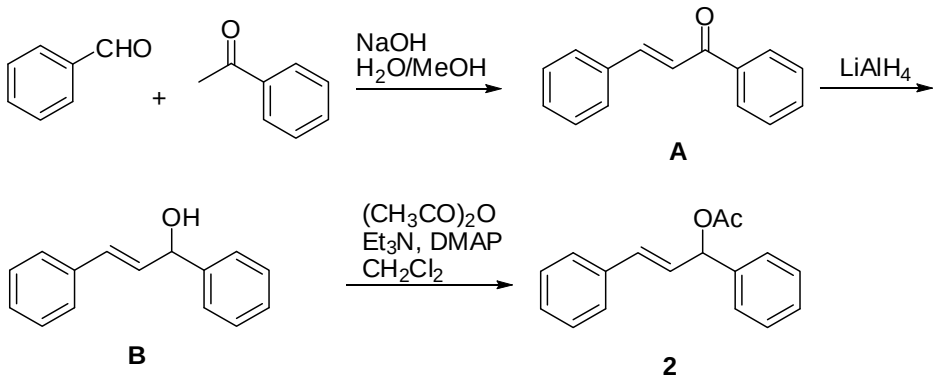
Experimental Section

General Information

All solvents were purified and dried according to standard methods prior to use. Reagents and catalysts were purchased from J&K Chemical Ltd or Alfa Aesar, and were used without further purification. Unless otherwise noted, the ^{1}H-NMR spectra were recorded at 400 or 600 MHz in $CDCl_3$ and the ^{13}C-NMR spectra were recorded at 100 or 150 MHz in $CDCl_3$ with TMS as internal standard. All shifts are given in ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 100 mesh. Melting points are uncorrected and were obtained on a Laboratory Devices Mel-Temp II instrument.

General procedure for the preparation of allylic acetate 2:



Synthesis of (*E*)- chalcone (A)[1a]

Acetophenone (1.2 mL, 10.4 mmol) and benzaldehyde (0.95 mL, 9.4 mmol) were added to a solution of 10% NaOH (8 mL) and methanol (3 mL) at 5 to 10℃ and stirred for additional 4 h at 25℃. The precipitate thus formed was collected by filtration and washed with water. The crude product was further purified by flash column chromatography on silica gel with ethyl acetate and petroleum as eluent (v/v =1:5) to give chalcone **A** as a light yellow solid (1.6 g, 82%). ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.82 (d, *J* = 15.7 Hz, 1H), 7.65 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.46 (m, 3H), 7.42 (dd, *J* = 4.9, 1.7 Hz, 3H).

Spectral data match those previously reported.[1b]

Synthesis of (*E*)-1, 3-diphenylprop-2-en-1-ol (B)[2a]

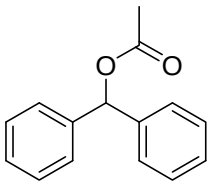
To a 5 mL THF solution of **A** (100mg, 0.48mmol) was added LAH (91 mg, 2.4 mmol) under stirring at -10 ^{o}C. LAH was added at such a rate that the solution temperature did not rise above -7 ^{o}C. The reaction mixture was then stirred until the starting material had disappeared as monitored by TLC. Water was then added dropwise to quench the reaction. THF was removed under reduced pressure, and the residue was extracted with dichloromethane (3 × 20 mL). The combined organic layers was dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography on silica gel with ethyl acetate and petroleum (v/v = 1:5) as eluent to give **B** as a white solid (90 mg, 90%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 4H), 7.33 – 7.26 (m, 3H), 7.22 (dd, *J* = 8.5, 5.8 Hz, 1H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.37 (dd, *J* = 15.9, 6.5 Hz, 1H), 5.37 (d, *J* = 6.5 Hz, 1H), 2.12 (brs, 1H). Spectral data match those previously reported.[2b]

Synthesis of (*E*)-1, 3-diphenylallyl acetate (2)[3]

DMAP (5.8 mg, 0.048 mmol) was added to a 3 mL DCM solution of **B** (100 mg, 0.48 mmol), Et_3N (1 mL, 1.2 mmol), and acetic anhydride (1 mL, 1.2 mmol). The reaction mixture was stirred at room temperature until **B** had disappeared as monitored by TLC. Ethyl acetate (30 mL) was added and the mixture was washed with water (3 × 30 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography on silica gel with ethyl acetate and petroleum (v/v = 1:5) as eluent to give **2** as colourless oil (110 mg, 91%). ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.34 (m, 6H), 7.31 (dd, *J* = 15.6, 7.8 Hz, 3H), 7.28 – 7.22 (m, 1H), 6.63 (d, *J* = 15.8 Hz, 1H), 6.44 (d, *J* = 6.9 Hz, 1H), 6.35 (dd, *J* = 15.8, 6.8 Hz, 1H), 2.14 (s, 3H). Spectral data match those previously reported.[3]

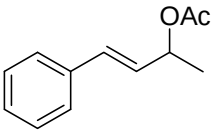
Following the similar procedures, allylic acetates 4 and 6 were also synthesized in high yield and purity.

Spectra data of Benzhydryl acetate (4):



Colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 4.2 Hz, 7H), 7.32 – 7.26 (m, 3H) 6.88 (s, 1H), 2.16 (s, 3H). Spectral data match those previously reported.[5]

Spetra data of (*E*)-4-Phenylbut-3-en-2-yl acetate (6):



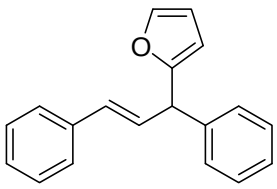
Colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.32 (dd, *J* = 10.0, 4.8 Hz, 2H), 7.24 (dd, *J* = 6.0, 3.5 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.19 (dd, *J* = 16.0, 6.7 Hz, 1H), 5.59 – 5.44 (m, 1H), 2.07 (s, 3H), 1.41 (d, *J* = 6.5 Hz, 3H). Spectral data match those previously reported.[3]

General procedure for the coupling of heteroarenes and allylic acetates (taking the reaction of 2 and furan 1a as a representative example):

A solution of allylic acetate **2** (100 mg, 0.4 mmol), $PdCl_2$ (1.4 mg, 2 mol %), and furan **1a**（0.13 mL, 1.98 mmol) in DCM (1.5 mL) was stirred in a sealed tube under reflux for 2 h. After completion of the reaction (monitored by TLC), the mixture was concentrated to a small volume, and was isolated by column chromatography on silica gel with dichloromethane and petroleum (v/v = 1:5) as eluent to give C-2 allylated product **3a** as a single isomer (74 mg,72%).

Note: 1.0 equivalent of heteroarenes were used except for the volatile furan, 2-methylfuran, pyrrole, and thiophene.

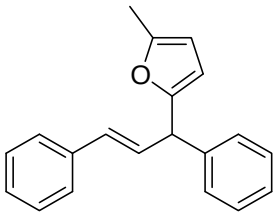
(*E*)-2-(1,3-Diphenylallyl)furan (3a)：



^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.0 Hz, 3H), 7.32 (d, *J* = 7.3 Hz, 2H),

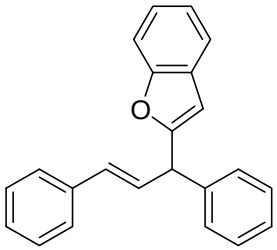
7.30–7.24 (m, 5H), 7.24–7.18 (m, 1H), 6.57 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.33 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.10 (d, *J* = 3.0 Hz, 1H), 4.90 (d, *J* = 7.4 Hz, 1H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 156.10, 141.82, 141.12, 137.01, 131.59, 129.74, 128.56, 128.47, 128.21, 127.43, 126.86, 126.36, 110.13, 106.74, 48.33.

(*E*)-2-(1,3-Diphenylallyl)-5-methylfuran (3b):



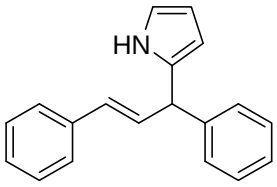
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.39–7.34 (m, 2H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.30–7.26 (m,2H), 7.26–7.18 (m, 4H), 6.56 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 5.95 (d, *J* = 3.0 Hz, 1H), 5.90 (d, *J* = 3.0 Hz, 1H), 4.84 (d, *J* = 7.4 Hz, 1H), 2.26 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.23, 151.41, 141.43, 137.16, 131.35, 130.14, 128.50, 128.47, 128.25, 127.35, 126.74, 126.36, 107.43, 105.97, 48.40, 13.59. Spectral data match those previously reported.[6]

(*E*)-2-(1, 3-Diphenylallyl)benzofuran (3c):



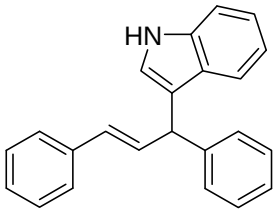
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.50 (dd, *J* = 6.9, 1.7 Hz, 1H), 7.43–7.38 (m, 3H), 7.36–7.31 (m, 4H), 7.31–7.27 (m, 2H), 7.26–7.16 (m, 4H), 6.65 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.48 (d, *J* = 14.3 Hz, 2H), 5.03 (d, *J* = 7.4 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.27, 155.03, 140.42, 136.87, 132.22, 129.01, 128.68, 128.53, 128.43, 128.36, 127.59, 127.11, 126.42, 123.64, 122.59, 120.60, 111.11, 103.96, 48.70. Spectral data match those previously reported.[6]

(*E*)-2-(1, 3-Diphenylallyl)-1*H*-pyrrole (3d):



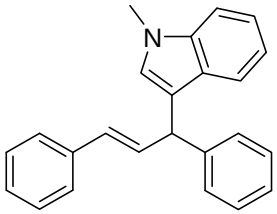
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.87 (br s, 1H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.35–7.31 (m, 2H), 7.29 (d, *J* = 7.3 Hz, 4H), 7.25–7.18 (m, 2H), 6.72 (s, 1H), 6.59 (dd, *J* = 15.8, 7.6 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.17 (d, *J* = 2.6 Hz, 1H), 5.97 (s, 1H), 4.87 (d, *J* = 7.6 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.11, 137.01, 133.00, 131.24, 131.10, 128.68, 128.51, 128.39, 127.43, 126.88, 126.34, 117.19, 108.40, 106.73, 48.07. Spectral data match those previously reported.[6]

(*E*)-3-(1, 3-Diphenylallyl)-1*H*-indole (3e):



^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.99 (br s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 13.8, 6.1 Hz, 5H), 7.32–7.27 (m, 3H), 7.25–7.13 (m, 4H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 1.5 Hz, 1H), 6.73 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 5.12 (d, *J* = 7.4 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.35, 137.46, 136.61, 132.51, 130.53, 128.45, 128.40, 127.13, 126.77, 126.35, 126.29, 122.57, 122.06, 119.84, 119.40, 118.63, 111.07, 46.15. Spectral data match those previously reported.[7]

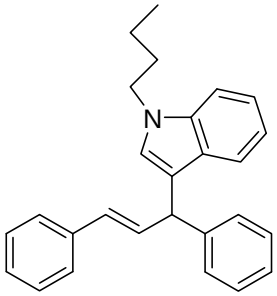
(*E*)-3-(1, 3-Diphenylallyl)-1-methyl-1*H*-indole (3f):



^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.9 Hz, 1H), 7.35 (dd, *J* = 14.3, 6.1 Hz, 3H), 7.32–7.27 (m, 3H), 7.27–7.16 (m, 6H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.75 (s, 1H), 6.73 (dd, *J* = 15.8, 7.2 Hz 2H), 6.44 (d, *J* = 15.8 Hz, 1H), 5.11 (d, *J* = 7.2 Hz, 1H),

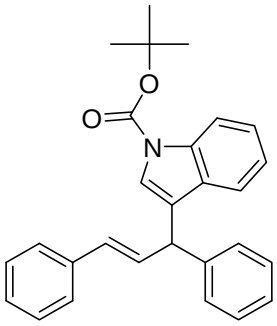
3.74 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.54, 137.52, 137.40, 132.70, 130.41, 128.45, 128.39, 127.34, 127.20, 127.10, 126.30, 121.61, 119.93, 118.86, 117.08, 109.15, 46.15, 32.66. Spectral data match those previously reported.[7]

(*E*)-1-Butyl-3-(1, 3-diphenylallyl)-1*H*-indole (3g):



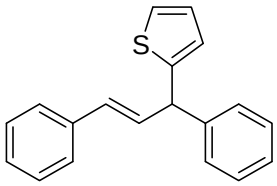
^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.38 (dd, *J* = 16.5, 7.7 Hz, 3H), 7.35 – 7.26 (m, 7H), 7.20 (ddd, *J* = 21.7, 14.7, 7.3 Hz, 3H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.80 (s, 1H), 6.72 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 5.11 (d, *J* = 7.4 Hz, 1H), 4.06 (t, *J* = 7.2 Hz, 2H), 1.89–1.73 (m, 2H), 1.41–1.26 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 143.57, 137.55, 136.69, 132.81, 130.35, 128.47, 128.44, 128.35, 127.27, 127.08, 126.29, 121.40, 119.99, 118.72, 116.87, 109.35, 46.21, 46.05, 32.35, 20.21, 13.70.

(*E*)-Tert-butyl 3-(1, 3-diphenylallyl)-1*H*-indole-1-carboxylate (3h):



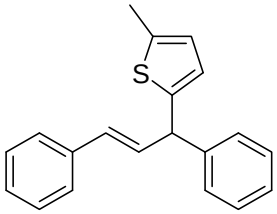
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 6.6 Hz, 1H), 7.36 (t, *J* = 5.1 Hz, 3H), 7.34–7.30 (m, 4H), 7.30–7.25 (m, 4H), 7.21 (dd, *J* = 13.1, 5.5 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.68 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 5.03 (d, *J* = 7.4Hz, 1H), 1.66 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.83, 142.05, 137.16, 135.77, 131.26, 131.16, 129.84, 128.53, 128.45, 128.37, 127.31, 126.66, 126.33, 124.30, 123.74, 122.99, 122.39, 120.06, 115.21, 83.59, 45.90, 28.15.

(*E*)-2-(1, 3-Diphenylallyl)thiophene (3i):



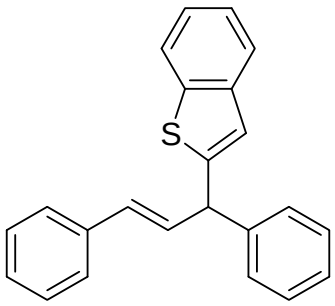
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40 (t, *J* = 6.1 Hz, 2H), 7.35 (dd, *J* = 8.9, 7.1 Hz, 4H), 7.32–7.25 (m, 4H), 7.24 (d, *J* = 5.1 Hz, 1H), 6.99 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.85 (d, *J* = 3.5 Hz, 1H), 6.68 (dd, *J* = 15.8, 7.6 Hz, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 5.10 (d, *J* = 7.6 Hz, 1H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 147.60, 143.15, 136.99, 131.93, 131.27, 128.59, 128.51, 128.21, 127.46, 126.88, 126.74, 126.41, 125.07, 124.34, 49.72.

(*E*)-2-(1, 3-Diphenylallyl)-5-methylthiophene (3j):



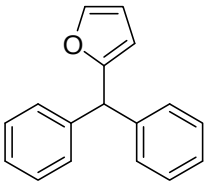
^{1}H-NMR (400 MHz, $CDCl_3$): δ7.37 (t, *J* = 6.5 Hz, 2H), 7.31 (dd, *J* = 10.7, 4.8 Hz, 5H), 7.28–7.24 (m, 2H), 7.24–7.18 (m, 1H), 6.65 – 6.56 (m, 3H), 6.44 (d, *J* = 15.8 Hz, 1H), 4.98 (d, *J* = 7.6 Hz, 1H), 2.42 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 145.11, 143.24, 138.85, 137.07, 132.03, 131.09, 128.53, 128.49, 128.19, 127.39, 126.80, 126.39, 124.80, 124.70, 49.86, 15.30.

(*E*)-2-(1,3-Diphenylallyl)benzo[b]thiophene(3k)



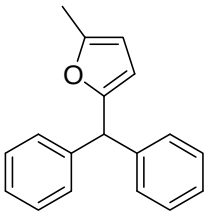
3k: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.37–7.23 (m, 12H), 7.13 (s, 1H), 6.72 (dd, *J* = 15.8, 7.4 Hz, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 5.21 (d, *J* = 7.4 Hz, 1H).

2-Benzhydrylfuran (5a):



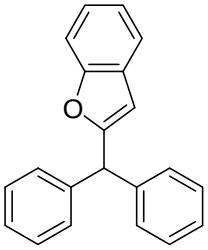
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 1.0, 1H), 7.30 (t, *J* = 8.0, 4H), 7.25–7.23 (m, 2H), 7.17 (d, *J* = 8.0, 4H), 6.31 (dd, *J* = 3.2, 2.0 Hz, 1H), 5.91 (d, *J* = 3.2 Hz, 1H), 5.45 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.69, 141.90, 141.78, 128.73, 128.42, 126.72, 110.06, 108.28, 50.87.

2-Benzhydryl-5-methylfuran (5b):



^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32–7.26 (m, 4H), 7.24–7.19 (m, 2H), 7.17 (m, 4H). 5.88 (d, *J* = 3.0 Hz, 1H), 5.75 (d, *J* = 3.0 Hz, 1H), 5.39 (s, 1H), 2.25 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.81, 151.48, 142.07, 128.77, 128.35, 126.59, 109.06, 105.91, 50.95, 13.62. Spectral data match those previously reported.[6]

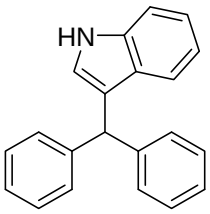
2-Benzhydrylbenzofuran (5c):



^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.46 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.41 (d, *J* = 8.1 Hz,

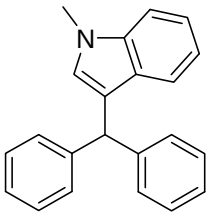
1H), 7.36–7.27 (m, 4H), 7.27–7.21 (m,7H), 7.21–7.15 (m, 1H), 6.27 (s, 1H), 5.58 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.89, 155.10, 141.00, 128.88, 128.55, 126.97, 123.72, 122.60, 120.62, 111.14, 105.63, 51.32. Spectral data match those previously reported.[6]

3-Benzhydryl-1*H*-indole (5d):



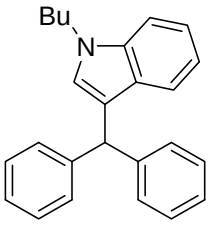
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.94 (br s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.30–7.18 (m, 11H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.56 (s, 1H), 5.67 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.91, 136.62, 128.97, 128.24, 126.93, 126.19, 124.03, 122.04, 119.86, 119.34, 111.02, 48.77. Spectral data match those previously reported.[8]

3-Benzhydryl-1-methyl-1*H*-indole (5e):



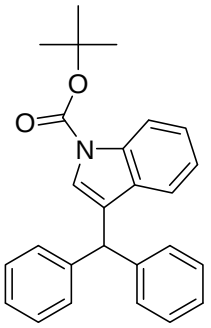
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.30–7.17 (m, 13H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.41 (s, 1H), 5.66 (s, 1H), 3.70 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.09, 137.42, 128.98, 128.69, 128.23, 127.35, 126.14, 121.60, 119.96, 118.80, 118.25, 109.08, 48.77, 32.61. Spectral data match those previously reported.[8]

3-Benzhydryl-1-butyl-1*H*-indole (5f):



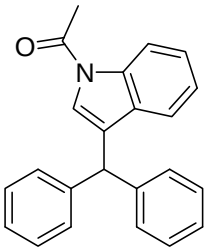
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31–7.26 (m, 3H), 7.26–7.14 (m, 10H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.45 (s, 1H), 5.66 (s, 1H), 4.02 (t, *J* = 7.2 Hz, 2H), 1.77–1.73 (m, 2H), 1.33–1.28 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.16, 136.72, 129.00, 128.22, 127.71, 126.11, 121.41, 120.04, 118.68, 118.13, 109.30, 48.80, 46.03, 32.33, 20.16, 13.68.

_t_-Butyl-3-benzhydryl-1_H_-indole-1-carboxylate (5g):



^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.31–7.20 (m, 9H), 7.18–7.14 (m, 2H), 7.10–7.04 (m, 2H), 7.01 (s, 1H), 5.56 (s, 1H),1.63 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.86, 142.60, 135.72, 130.10, 128.88, 128.41, 126.52, 125.23, 124.28, 124.18, 122.37, 120.14, 115.16, 83,59, 48.58, 28.14.

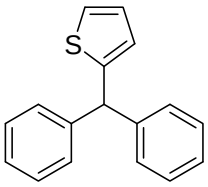
1-(3-benzhydryl-1_H_-indol-1-yl)ethanone (5h):



^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 7.6 Hz, 1H), 7.34–7.27 (m, 5H), 7.25–7.22 (m, 6H), 7.16–7.13 (m, 2H), 6.75 (s, 1H), 5.30 (s, 1H), 2.49 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 168.44, 142.29, 136.36, 130.04, 128.88, 128.54,

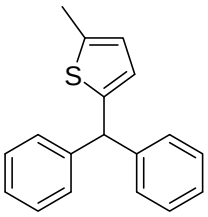
126.72, 126.22, 125.27, 124.54, 123.44, 120.07, 116.58, 48.58, 23.95.

2-Benzhydrylthiophene (5i):



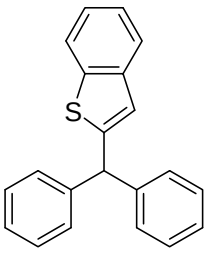
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32–7.28 (m, 5H), 7.25–7.20 (m, 6H), 6.93 (dd, *J* = 5.2, 3.6 Hz 1H), 6.69 (d, *J* = 3.6 Hz 1H), 5.68 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 147.89, 143.78, 128.96, 128.82, 128.37, 126.69, 126.54, 126.41, 126.34, 124.50, 52.11.

2-Benzhydryl-5-methylthiophene (5j):



^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31–7.28 (m, 4H), 7.24–7.21 (m, 4H), 6.57 (d, *J* = 4.0 Hz 1H), 6.46 (d, *J* = 4.0 Hz 1H), 5.58 (s, 1H), 2.41 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 145.40, 143.84, 138.98, 128.97, 128.81, 128.32, 126.60, 126.10, 124.52, 52.26, 15.30.

2-Benzhydrylbenzo[b]thiophene (5k):

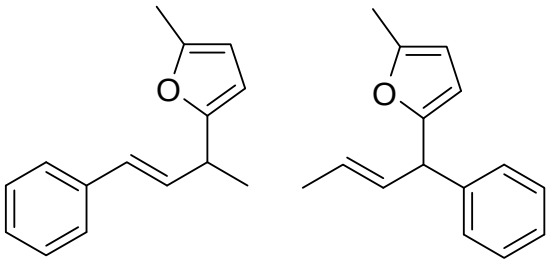


^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.85–7.83 (d, *J* = 8.0 Hz 1H), 7.47 (d, *J* = 8.0 Hz 1H) 7.31–7.21 (m, 8H), 7.18 (d, *J* =7.0 Hz 4H), 6.72 (s, 1H), 5.75 (s, 1H). ^{13}C-NMR (100

MHz, $CDCl_3$): δ 142.63, 140.67, 139.08, 138.46, 129.07, 128.46, 126.58, 125.10, 124.22, 123.90, 122.73, 122.70,122.12, 51.37.

(*E*)-2-Methyl-5-(4-phenylbut-3-en-2-yl)furan (7a) and

(*E*)-2-Methyl-5-(1-phenylbut-2-enyl)furan (8a)

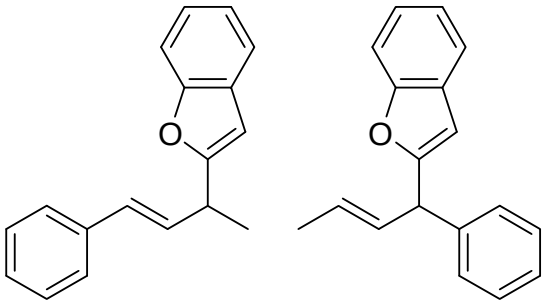


7a (major) **8a (minor)**

7a (major): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.0 Hz, 2H), 7.20 (d, *J* = 4.0 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.28 (dd, *J* = 15.8, 7.3 Hz, 1H), 5.91 (s, 1H), 5.87 (s, 1H), 3.69 – 3.54 (m, 1H), 2.26 (s, 3H), 1.42 (d, *J* = 6.9 Hz, 3H). **8a** (minor): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.0 Hz, 2H), 7.20 (d, *J* = 4.0 Hz, 1H), 5.91 (s, 1H), 5.87 (s, 1H), 5.79 (dd, *J* =14.8, 7.3 Hz, 1H), 5.49 (td, *J* = 12.5, 5.7 Hz, 1H), 4.61 (d, *J* = 7.1 Hz, 1H), 2.23 (s, 3H), 1.71 (d, *J* = 6.0 Hz, 3H). Spectral data match those previously reported.[6]

(*E*)-2-(4-Phenylbut-3-en-2-yl)benzofuran(7b) and

(*E*)-2-(1-Phenylbut-2-enyl)benzofuran(8b)



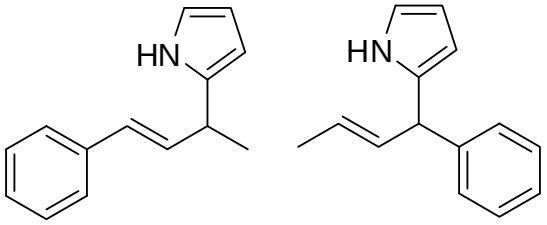
7b (major) **8b (minor)**

7b (major)**:** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.56–7.17 (m, 9H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.49 (s, 1H), 6.40 (dd, *J* = 15.9, 7.3 Hz, 1H), 3.94–3.76 (m, 1H), 1.58 (d, *J* = 7.0 Hz, 3H). **8b** (minor): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.56–7.17 (m, 9H), 6.46 (s, 1H),

5.95 (dd, *J* = 15.3, 7.5 Hz, 1H), 5.61 (m, 1H), 4.84 (d, *J* = 7.4 Hz, 1H), 1.78 (d, *J* = 6.6 Hz, 3H). Spectral data match those previously reported.[6]

(*E*)-2-Methyl-5-(4-phenylbut-3-en-2-yl)-1H-pyrrole (7c) and

(*E*)-2-Methyl-5-(1-phenylbut-2-enyl)-1H-pyrrole (8c)

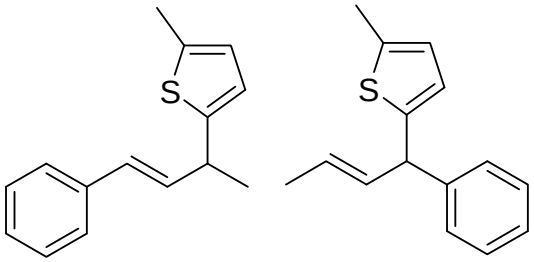


7c (major) **8c (minor)**

7c (major): ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.99 (br s, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.33–7.27 (m, 2H), 7.26–7.17 (m, 2H), 6.71 (s, 1H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.27 (dd, *J* = 15.8, 7.9 Hz, 1H), 6.18 (dd, *J* = 5.7, 2.8 Hz, 1H), 6.02 (s, 1H), 3.68–3.63 (m, 1H), 1.47 (d, *J* = 6.9 Hz, 3H). **8c** (minor): δ ^{1}H-NMR(600 MHz, $CDCl_3$) 7.81 (br s, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.33–7.27 (m, 2H), 7.26–7.17 (m, 2H), 6.68 (s, 1H), 6.15 (dd, *J* = 5.6, 2.8 Hz, 1H), 5.89 (s, 1H), 5.85 (dd, *J* = 15.1, 7.9 Hz, 1H), 5.54–5.50 (m, 1H), 4.64 (d, *J* = 7.7 Hz, 1H), 1.72 (d, *J* = 6.4 Hz, 3H). Spectral data match those previously reported.[6]

(*E*)-2-Methyl-5-(4-phenylbut-3-en-2-yl)thiophene(7d) and

(*E*)-2-Methyl-5-(1-phenylbut-2-enyl)thiophene (8d)



7d (major) **8d (minor)**

7d (major): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 6.7 Hz, 2H), 7.21 (d, *J* = 6.6 Hz, 1H), 6.63 (s, 1H), 6.58 (s, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.31 (dd, *J* = 15.5, 7.2 Hz, 1H), 3.92–3.70 (m, 1H), 2.43 (s, 3H), 1.49 (d, *J* = 6.4 Hz, 3H). **8d** (minor): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 6.7 Hz, 2H), 7.21 (d, *J* = 6.6 Hz, 1H), 6.63 (s, 1H), 6.58 (s, 1H), 5.88 (dd, *J* = 14.8,

7.3 Hz, 1H), 5.65–5.45 (m, 1H), 4.75 (d, *J* = 7.3 Hz, 1H), 2.41 (s, 3H), 1.72 (d, *J* = 6.1 Hz, 3H).

References:

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3. A. V. Malkov, I. R. Baxendale, D. J. Mansfield and P. Kocovsky, *J. Chem. Soc. Perkin Trans.*, 2001, **1**, 1234–1240.
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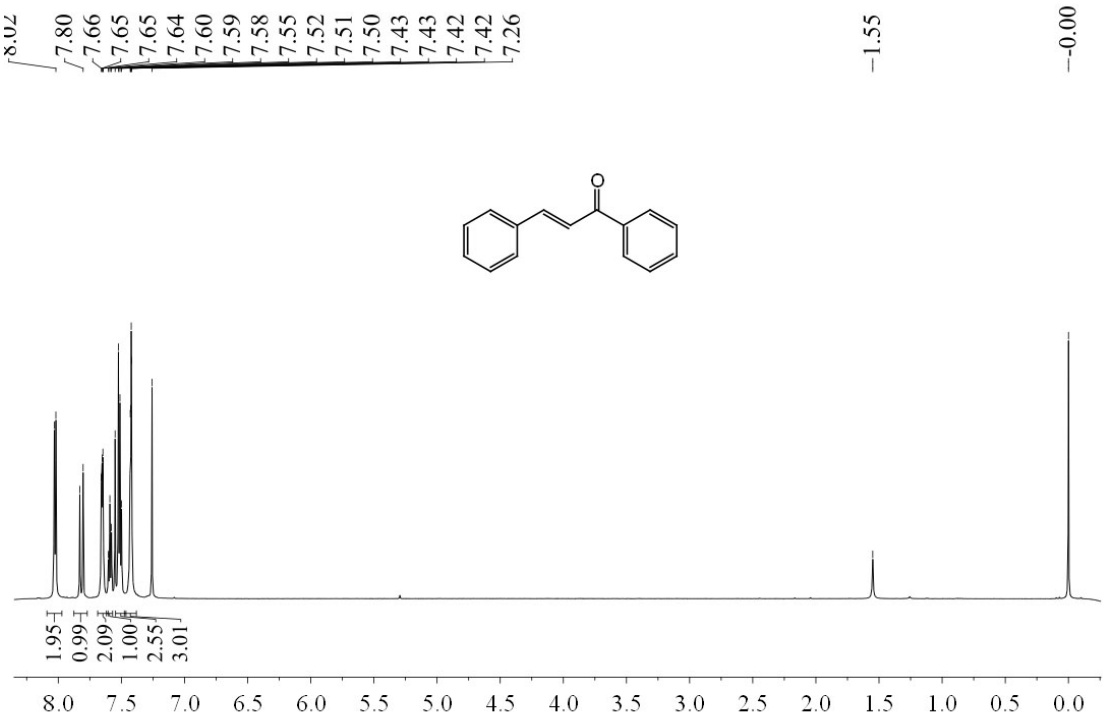

Figure S1. ^{1}H-NMR spectrum of compound **A**

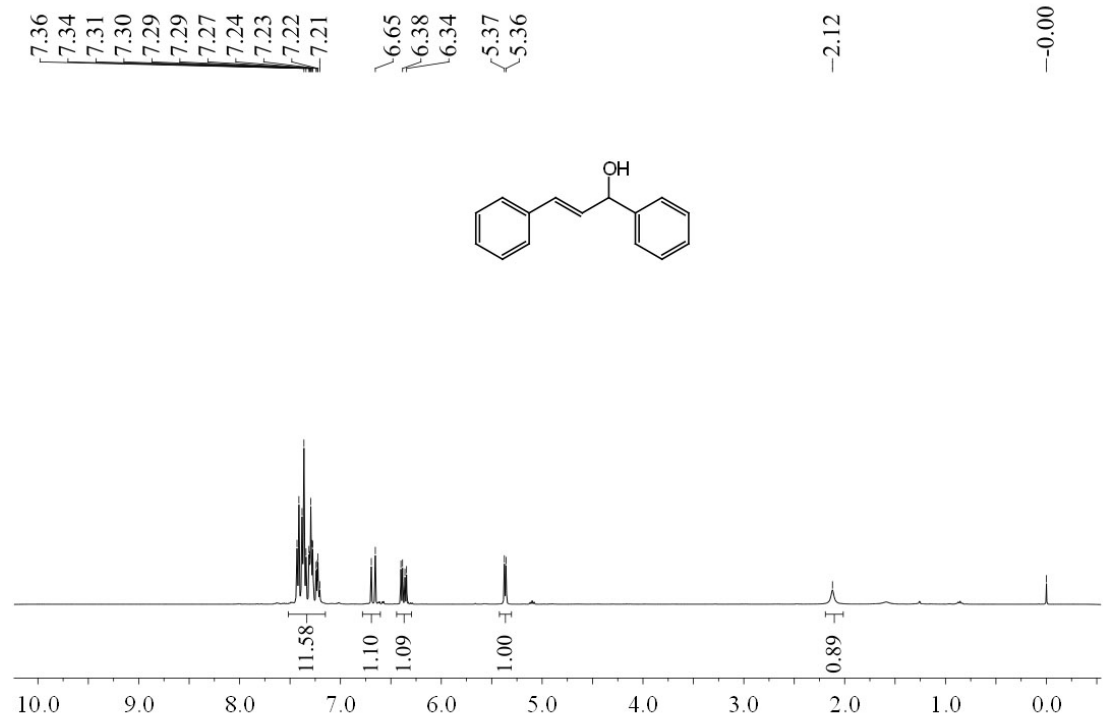

Figure S2. ^{1}H-NMR spectrum of compound **B**

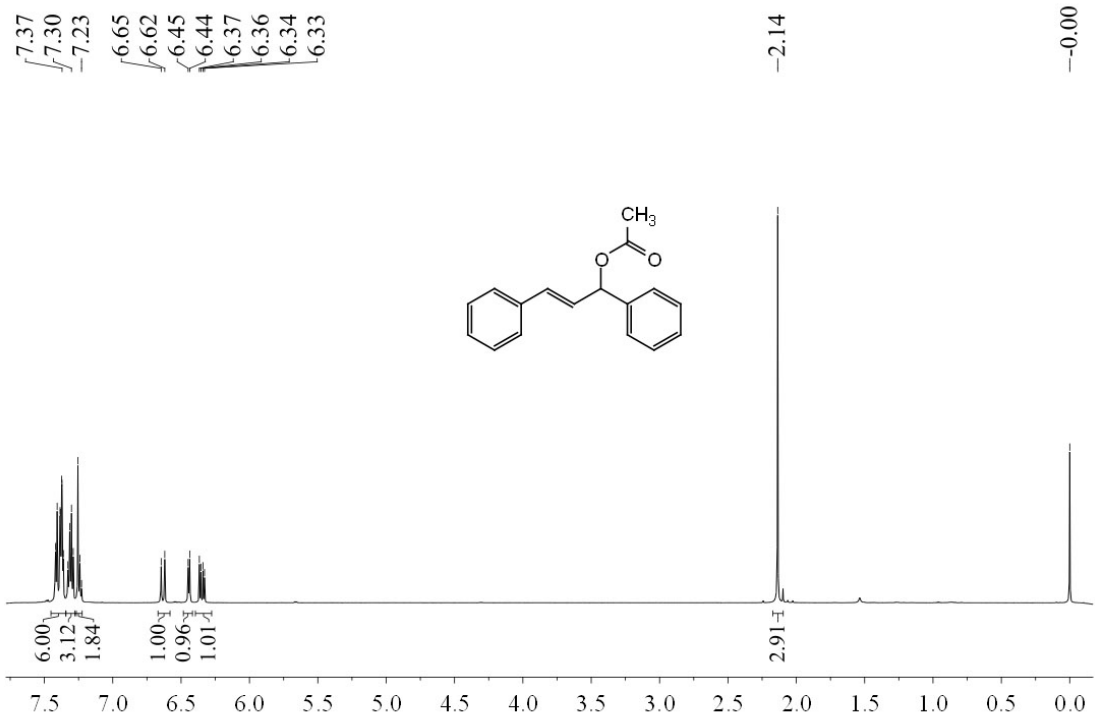

Figure S3. [1]H-NMR spectrum of compound **2**

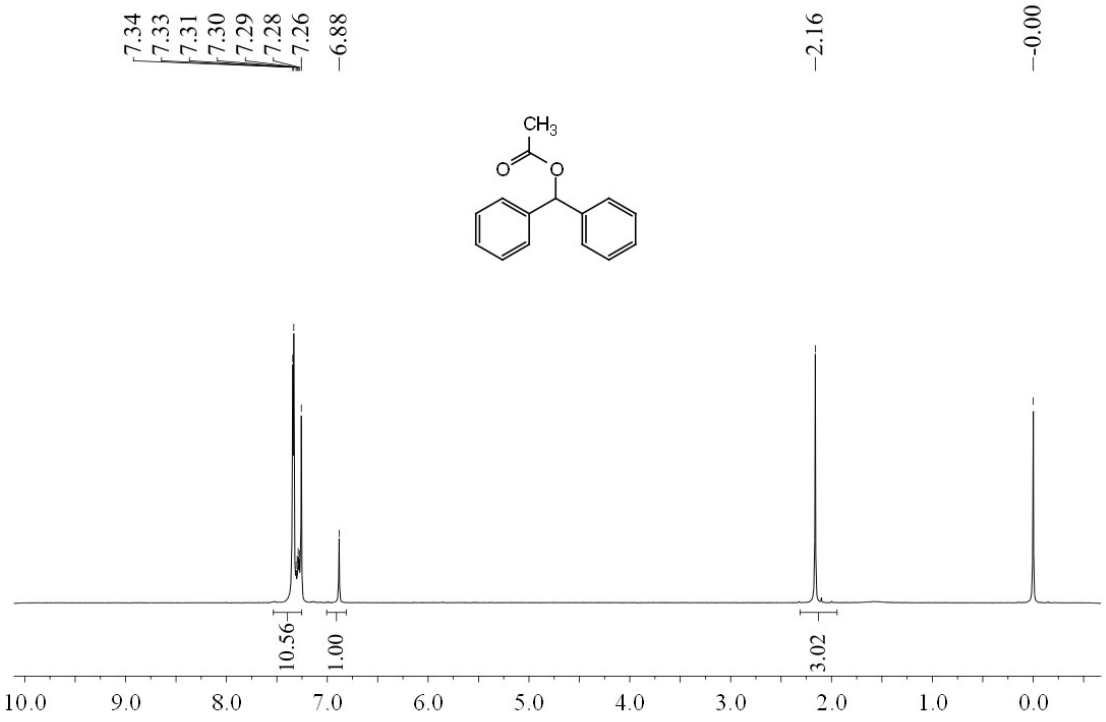

Figure S4. [1]H-NMR spectra of compound **4**

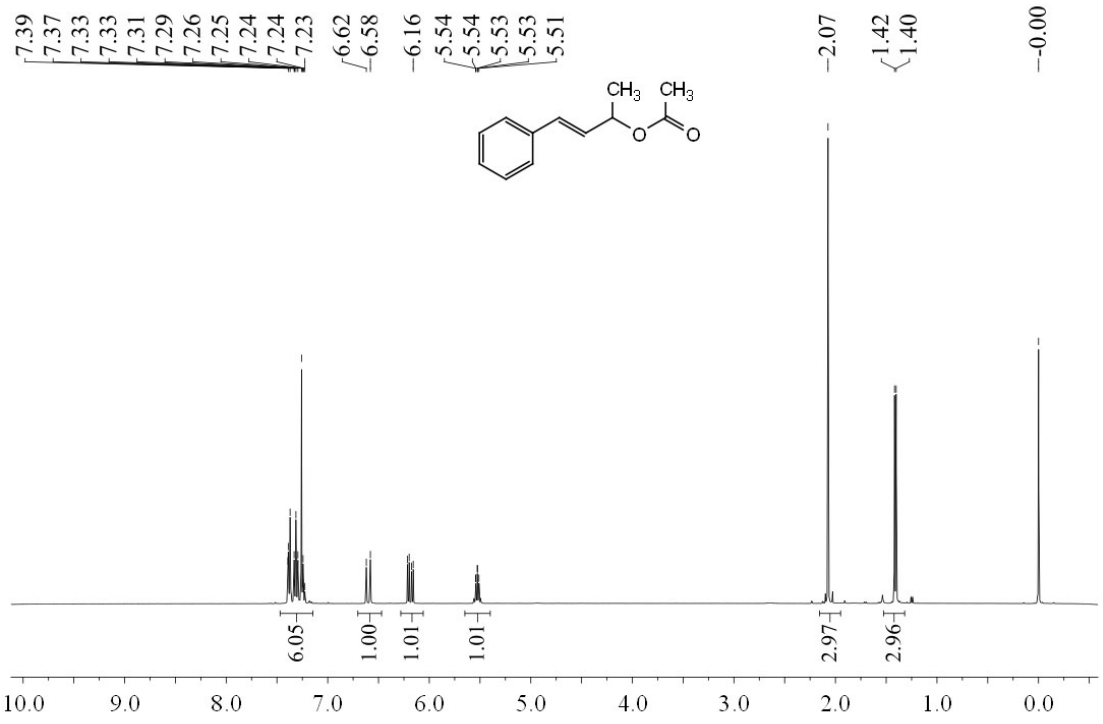

Figure S5. ^{1}H-NMR spectrum of compound **6**

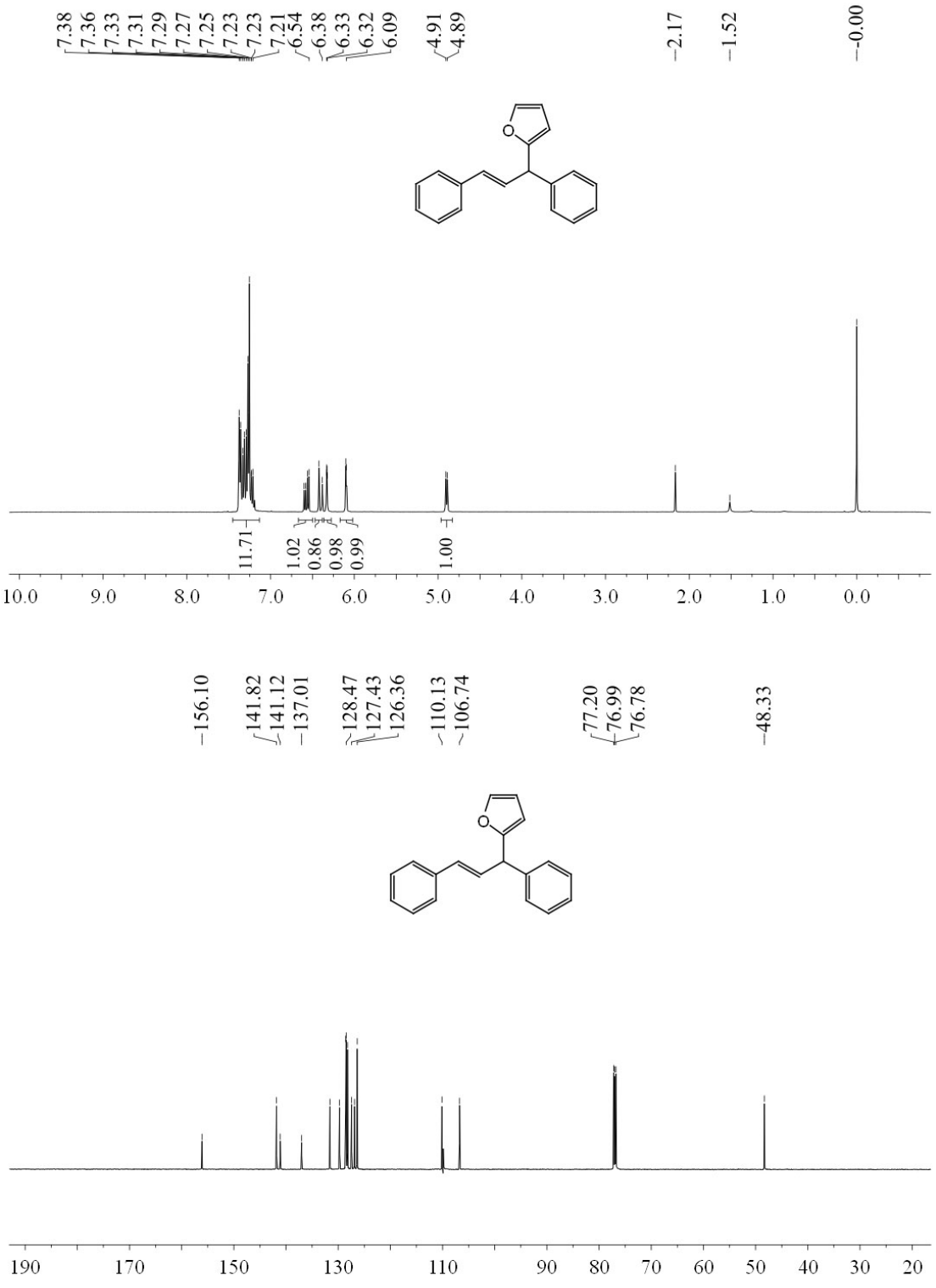

Figure S6. ^{1}H-(upper) and ^{13}C-(bottom) spectra of compound **3a**

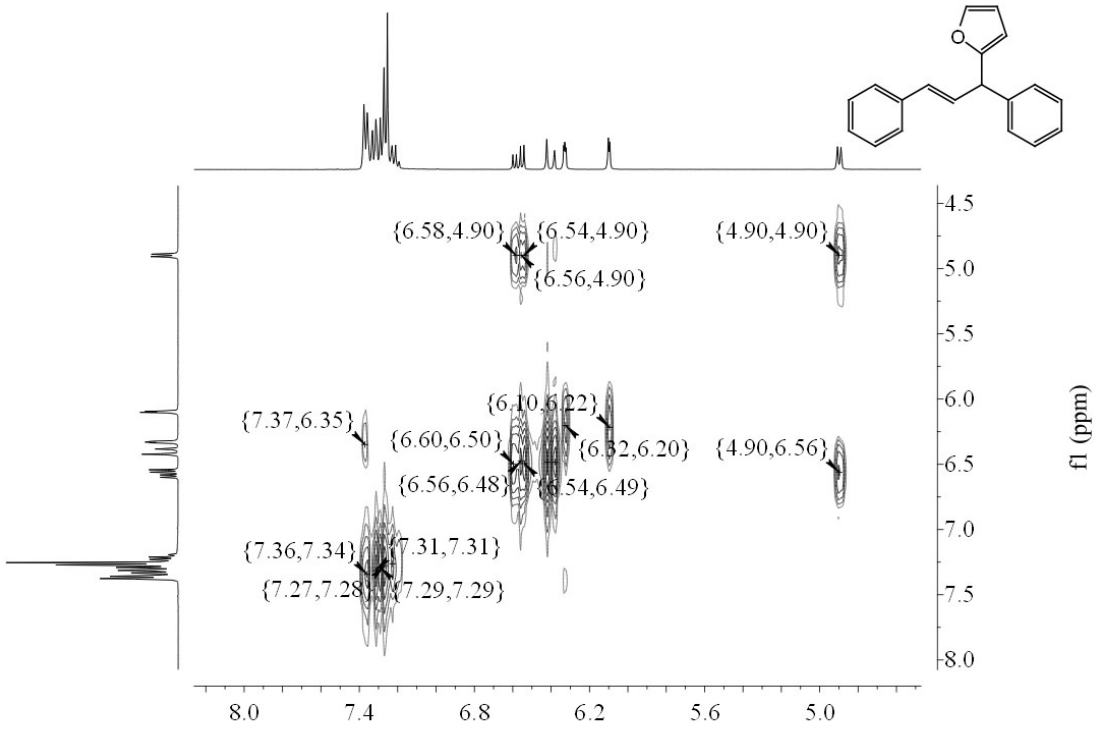

Figure S7. ^{1}H-^{1}H COSY spectrum of compound **3a**

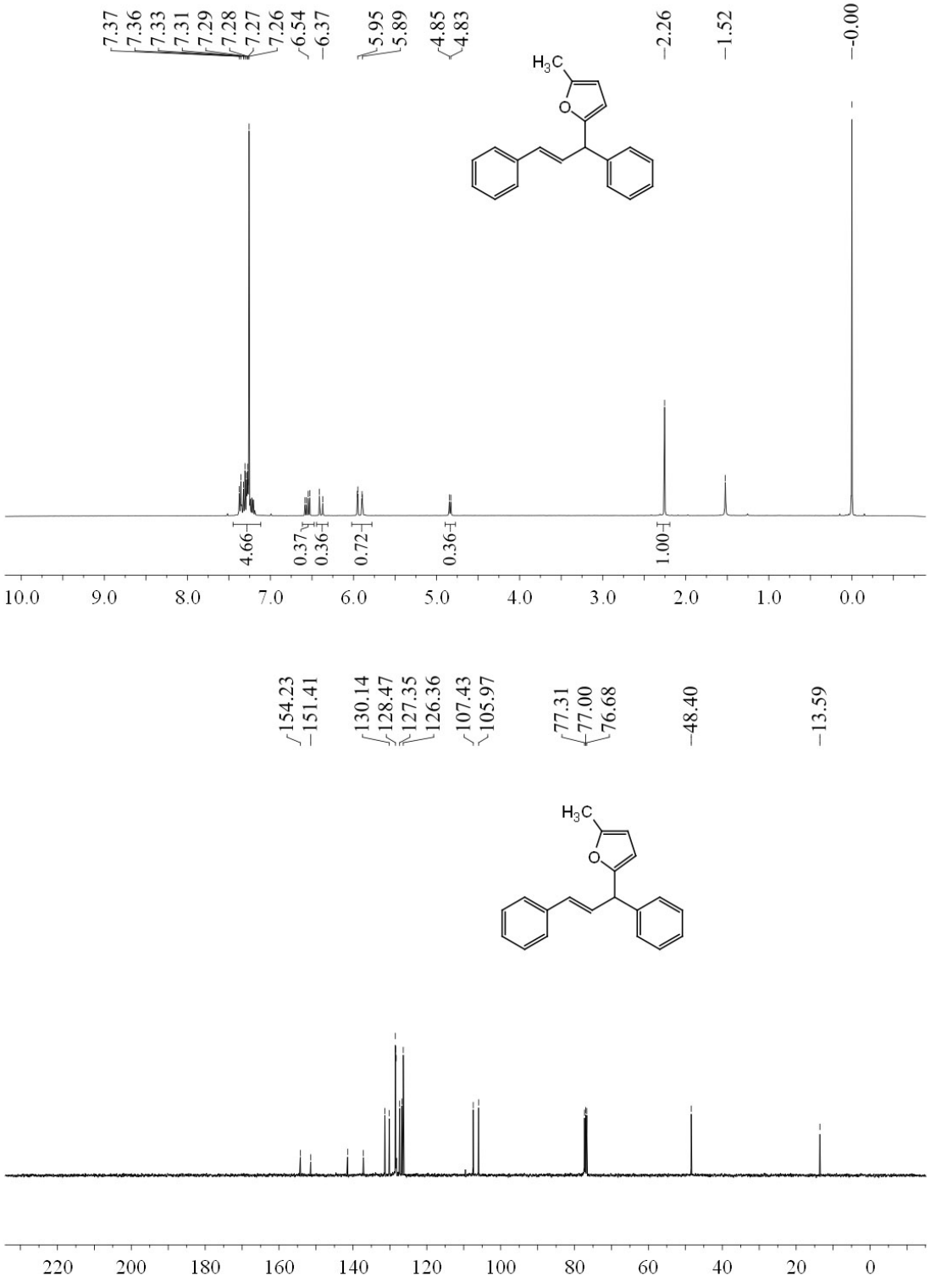

Figure S8. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **3b**

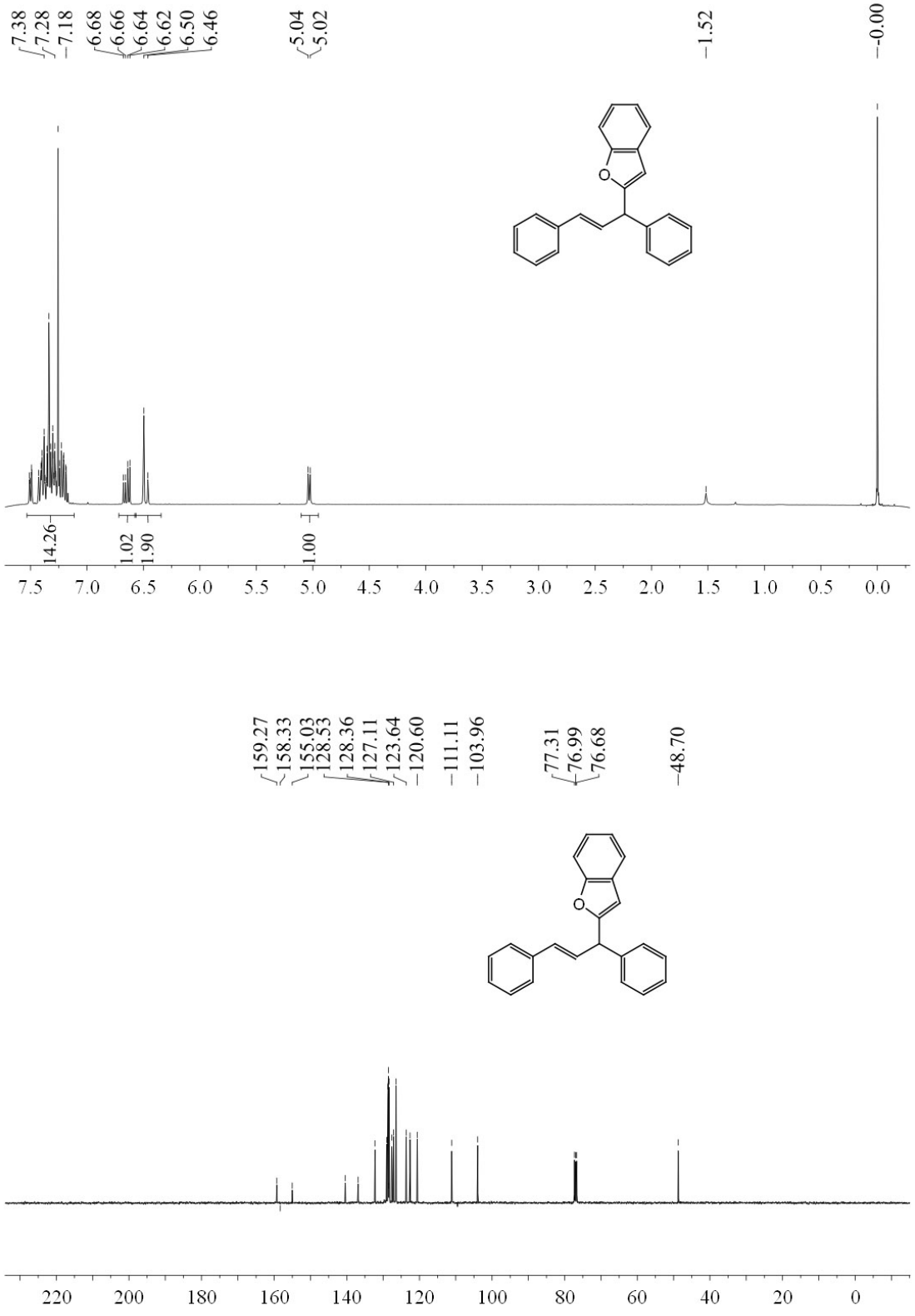

Figure S9. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **3c**

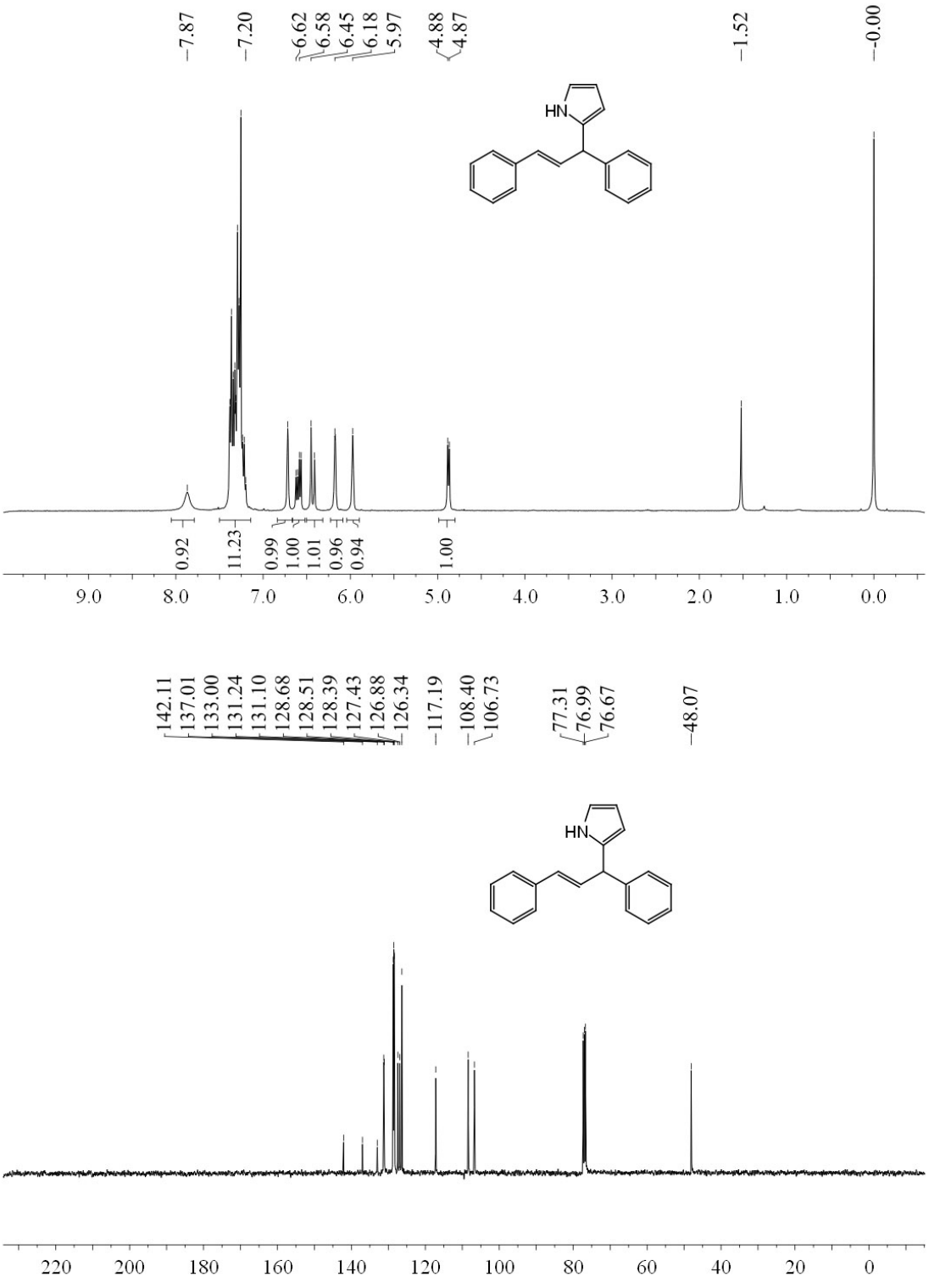

Figure S10. ^{1}H-(upper) and ^{13}C-(bottom) spectra of compound **3d**

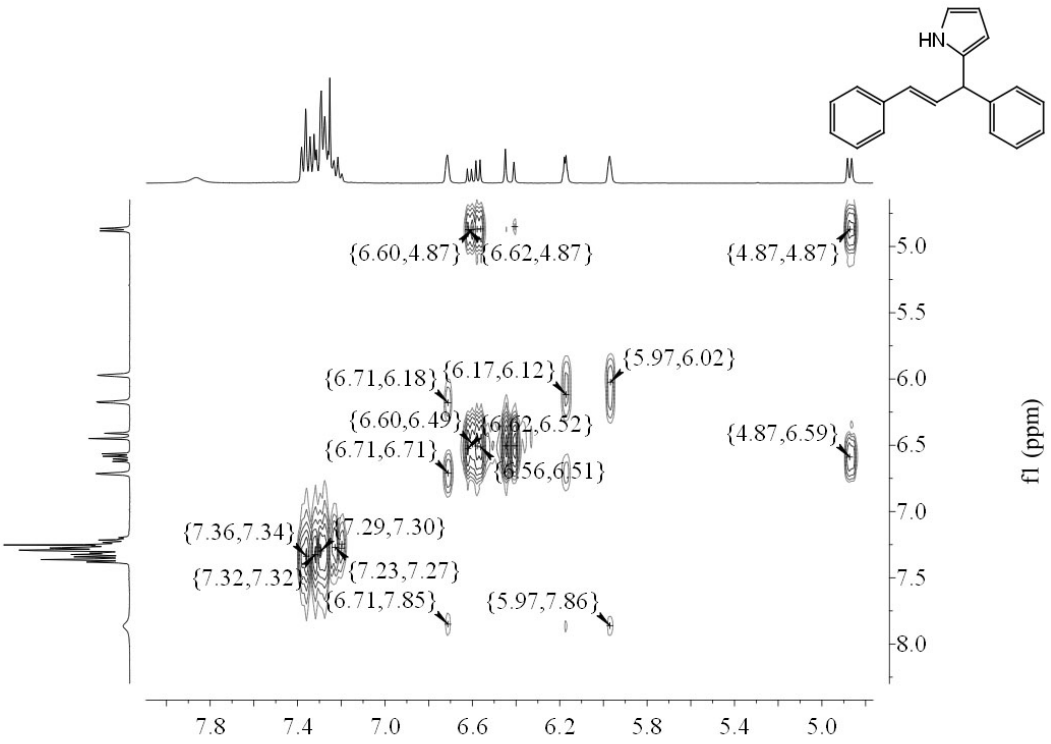

Figure S11. ^{1}H-^{1}H COSY spectra of compound **3d**

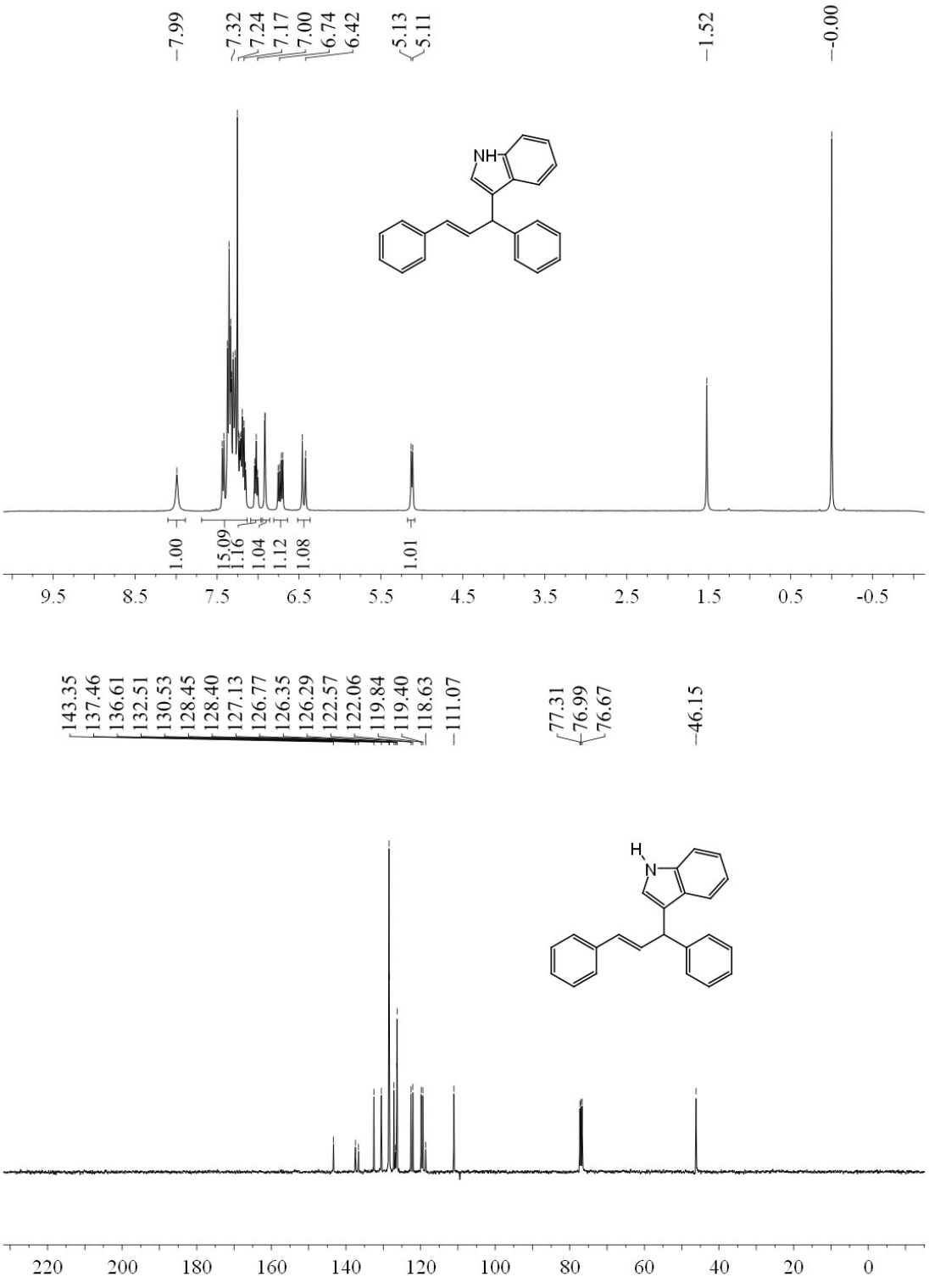

Figure S12. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **3e**

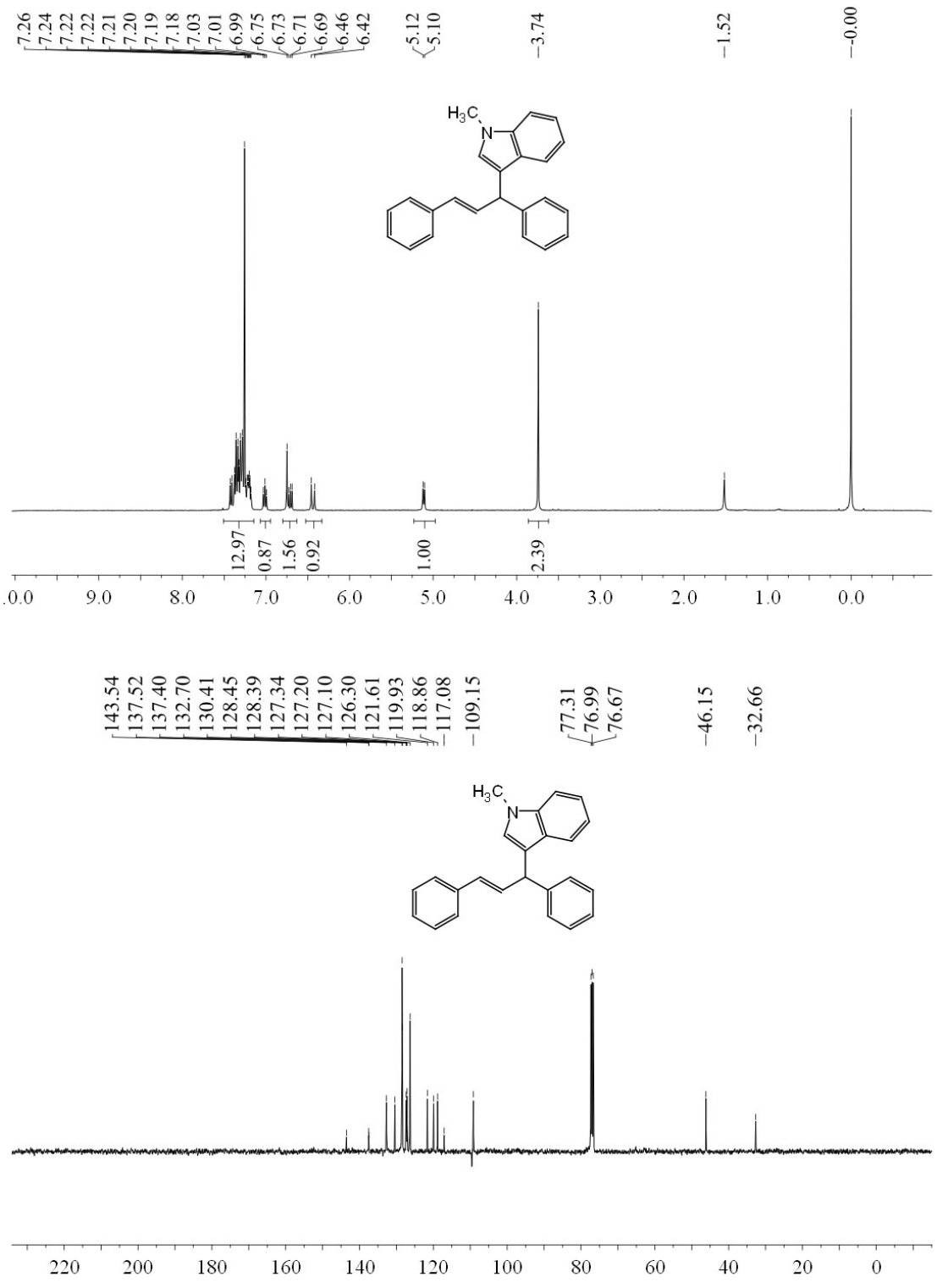

Figure S13. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **3f**

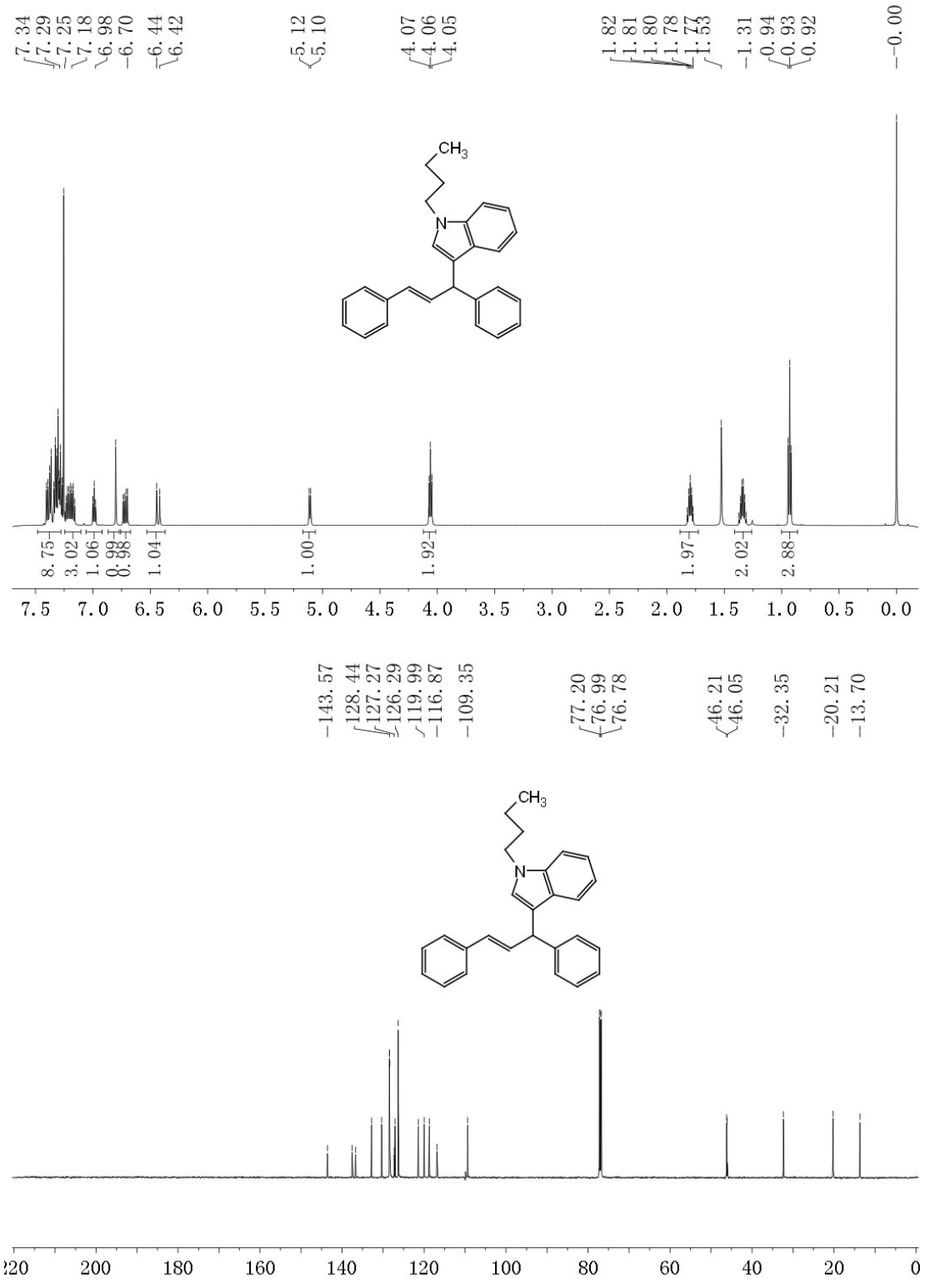

Figure S14. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **3g**

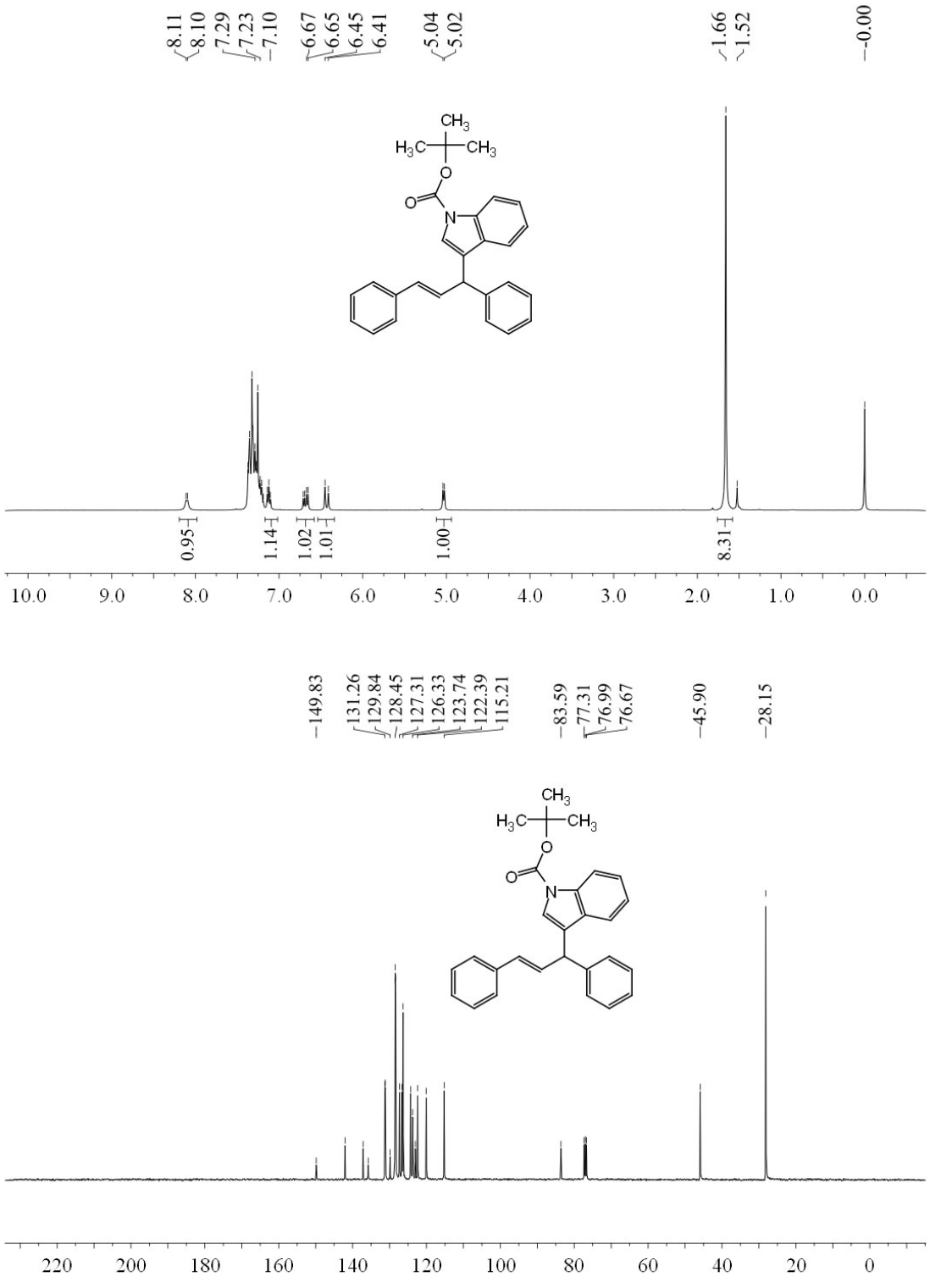

Figure S15. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **3h**

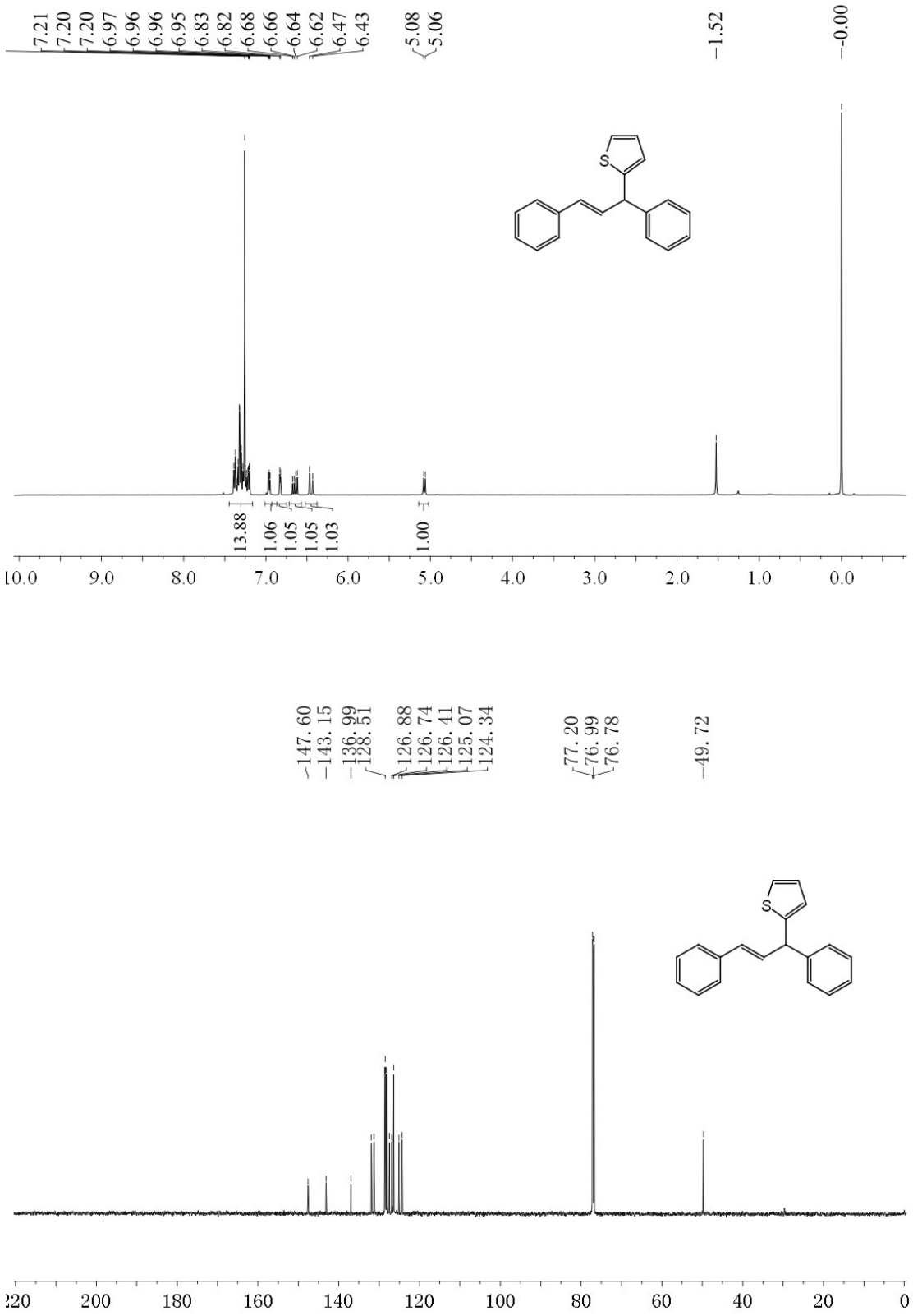

Figure S16. ^{1}H-(upper) and ^{13}C-(bottom) spectra of compound **3i**

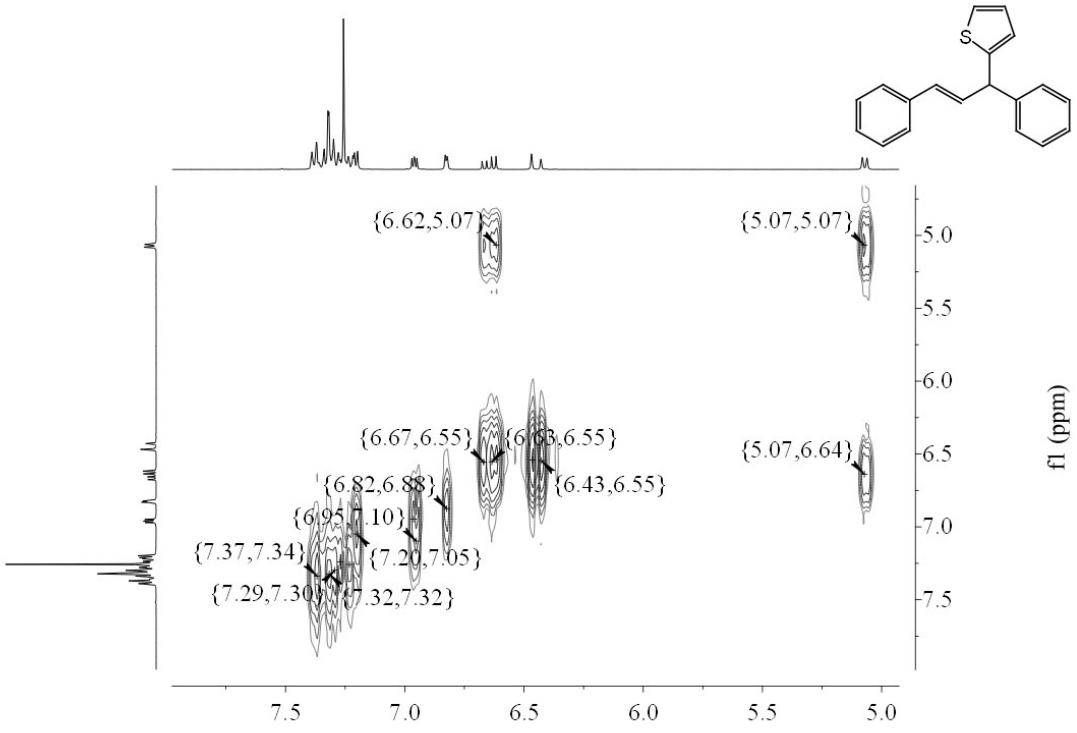

Figure S17. ^{1}H-^{1}H COSY spectra of compound **3i**

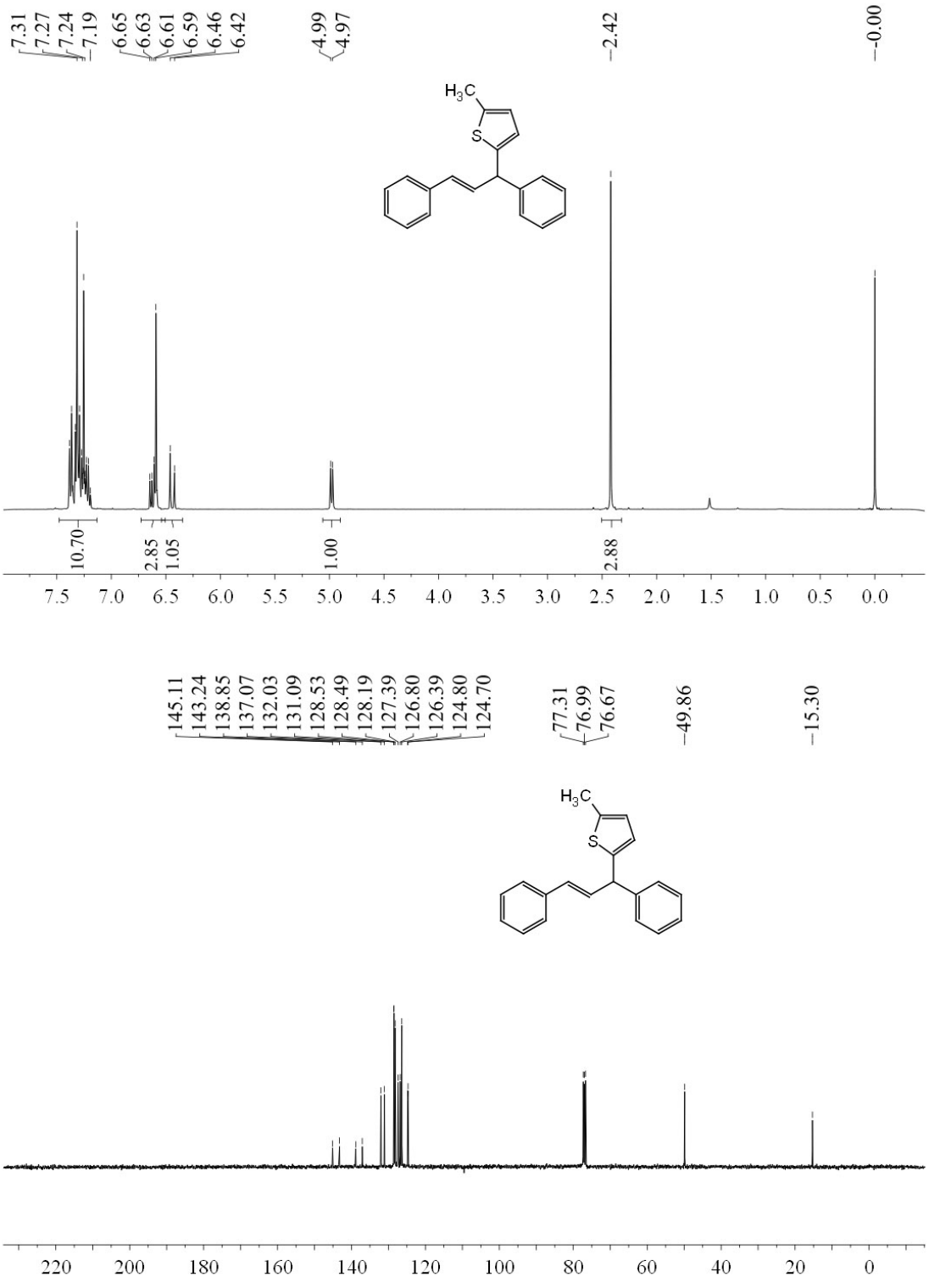

Figure S18. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **3j**

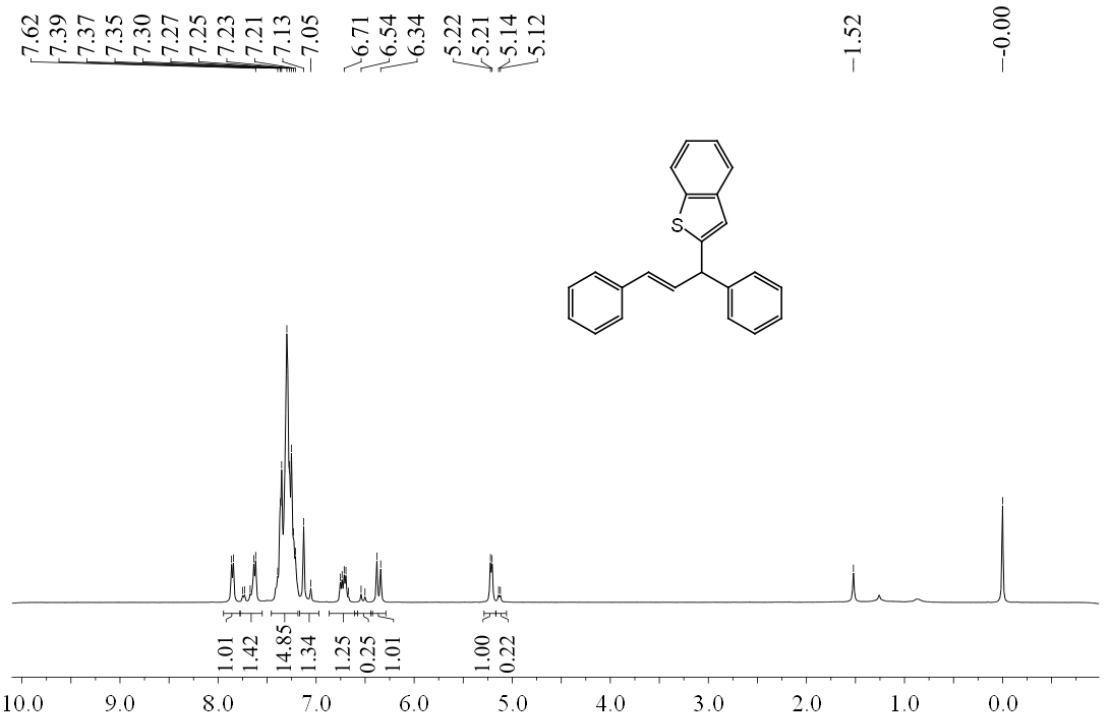

Figure S19. ^{1}H-NMR spectrum of compound **3k**

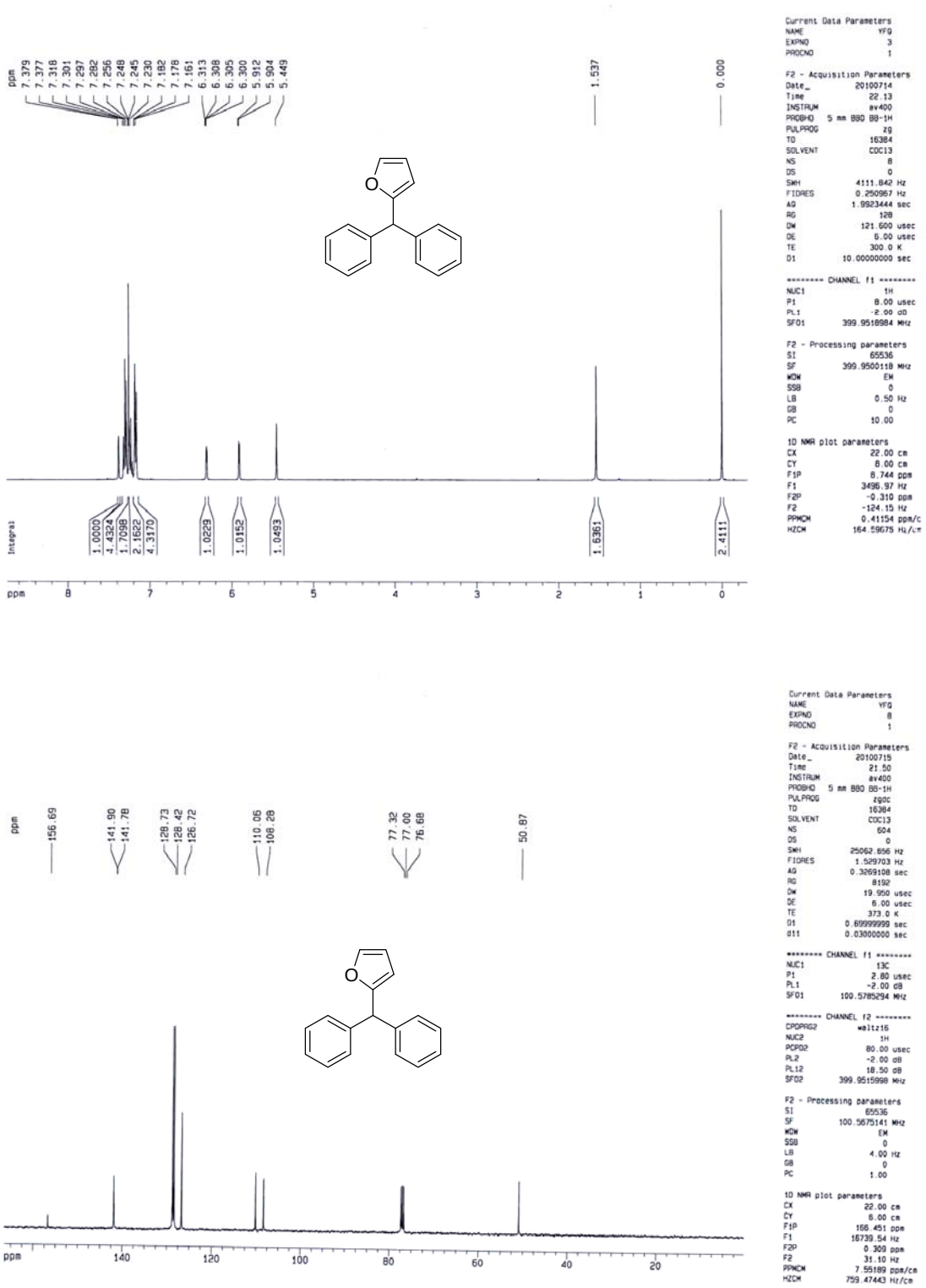

Figure S20. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **5a**

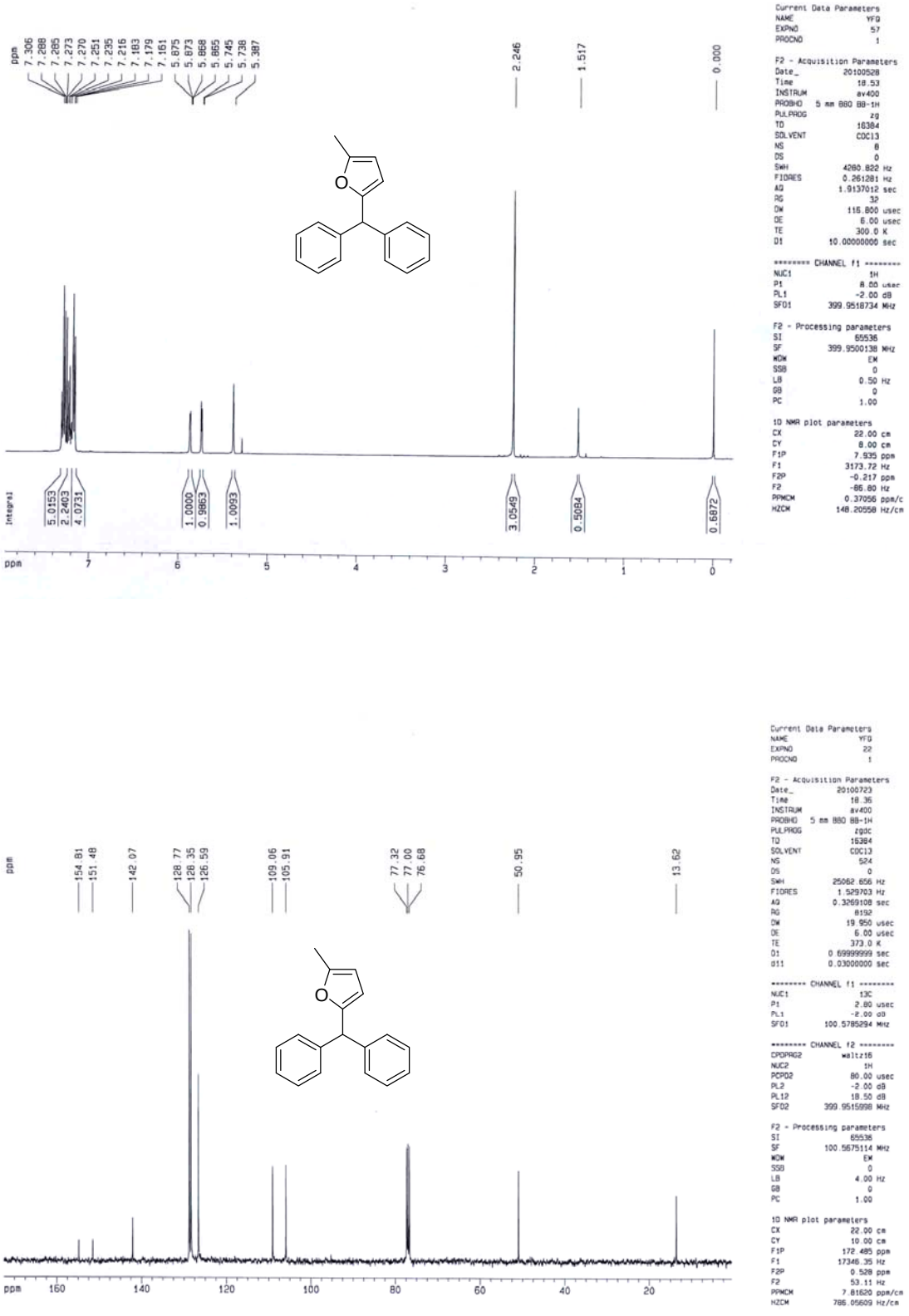

Figure S21. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **5b**

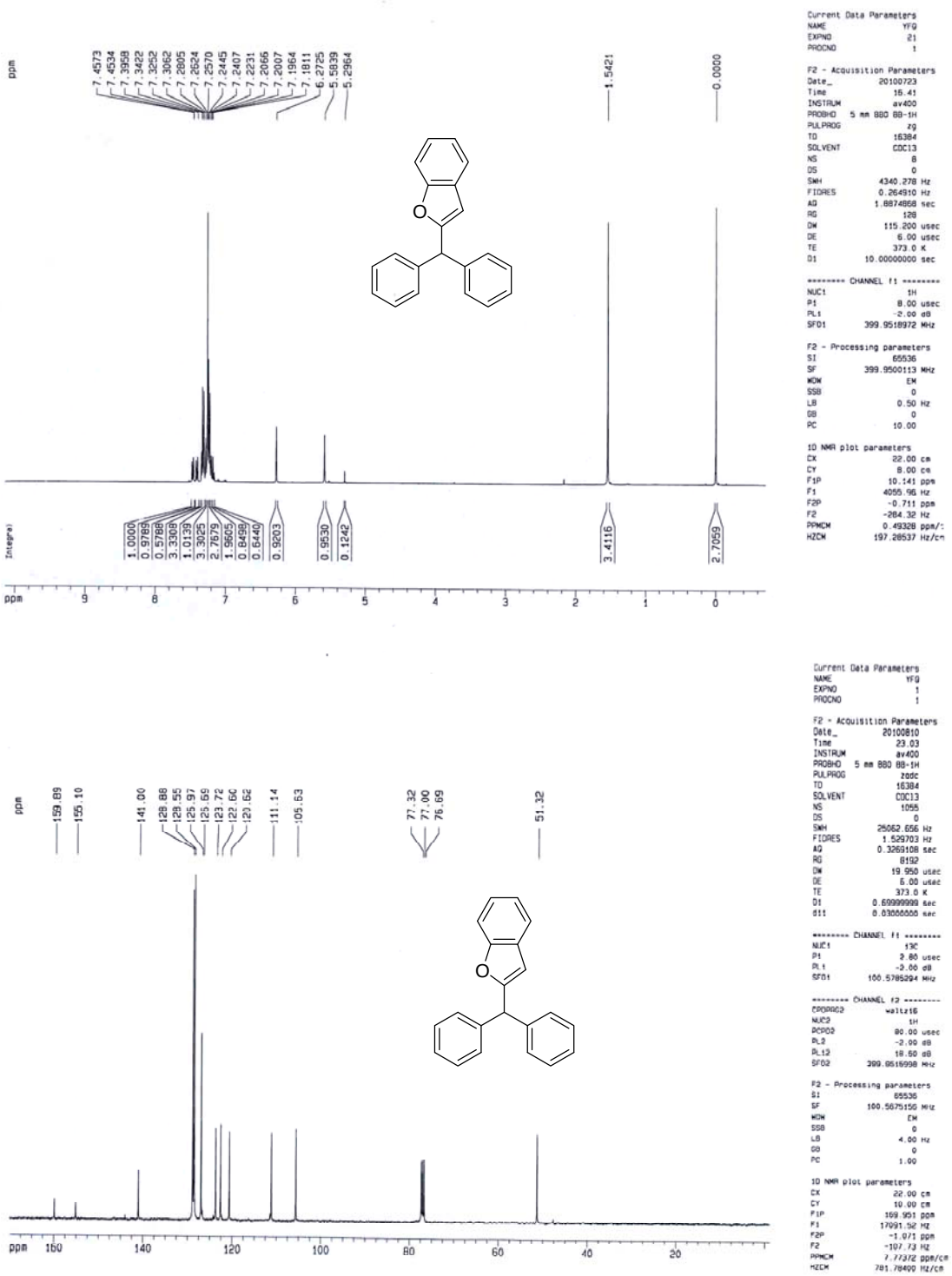

Figure S22. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **5c**

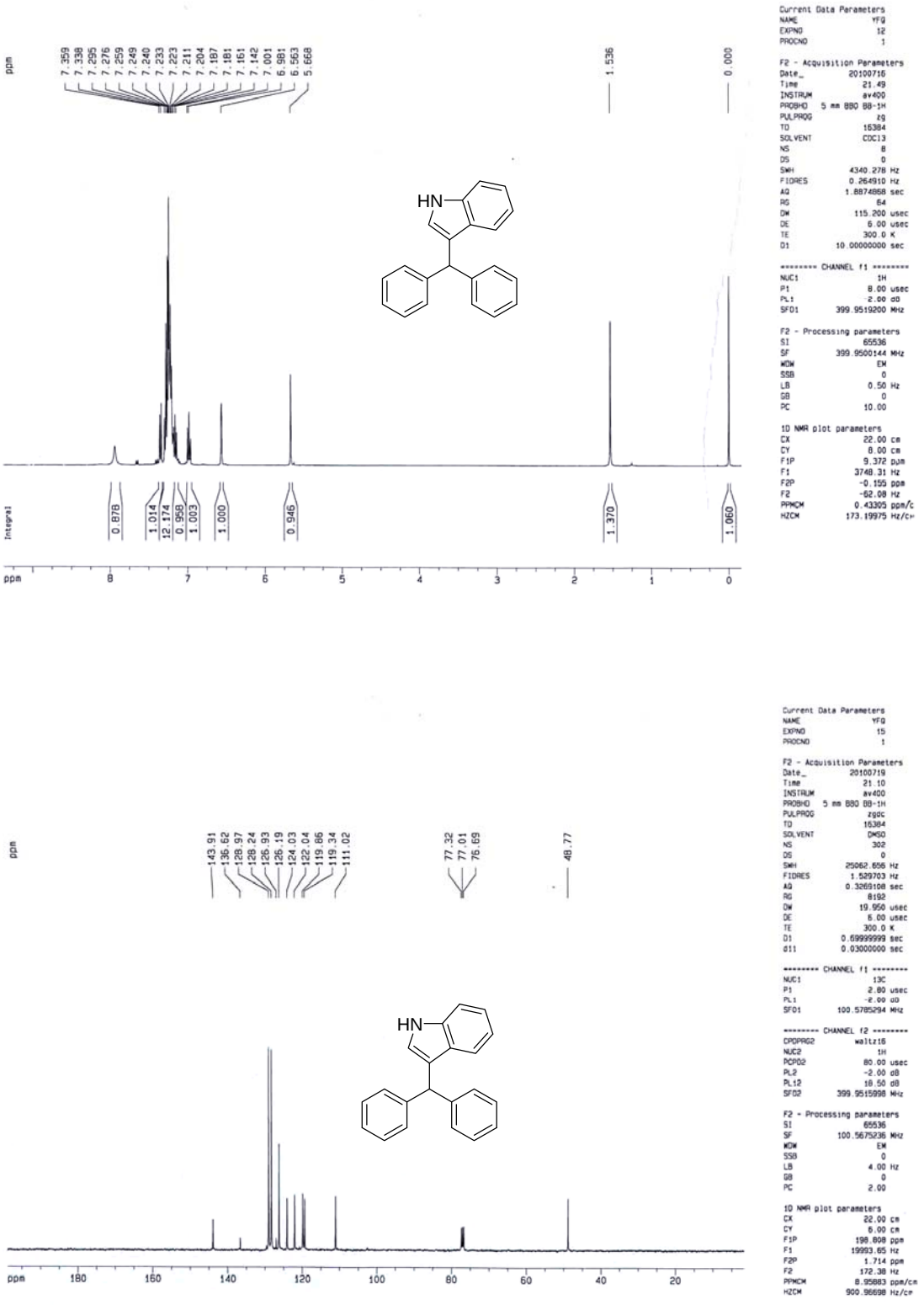

Figure S23. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **5d**

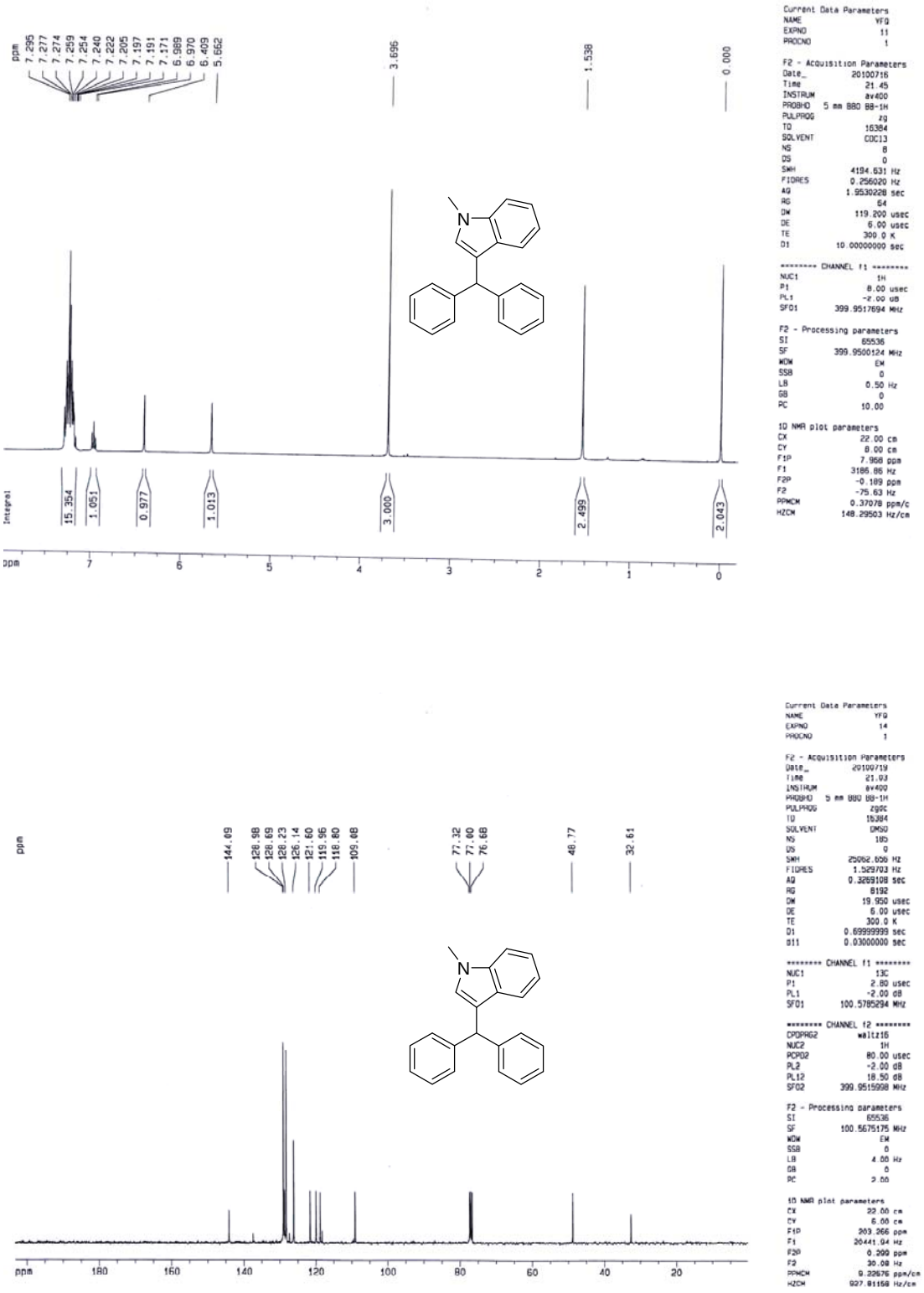

Figure S24. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **5e**

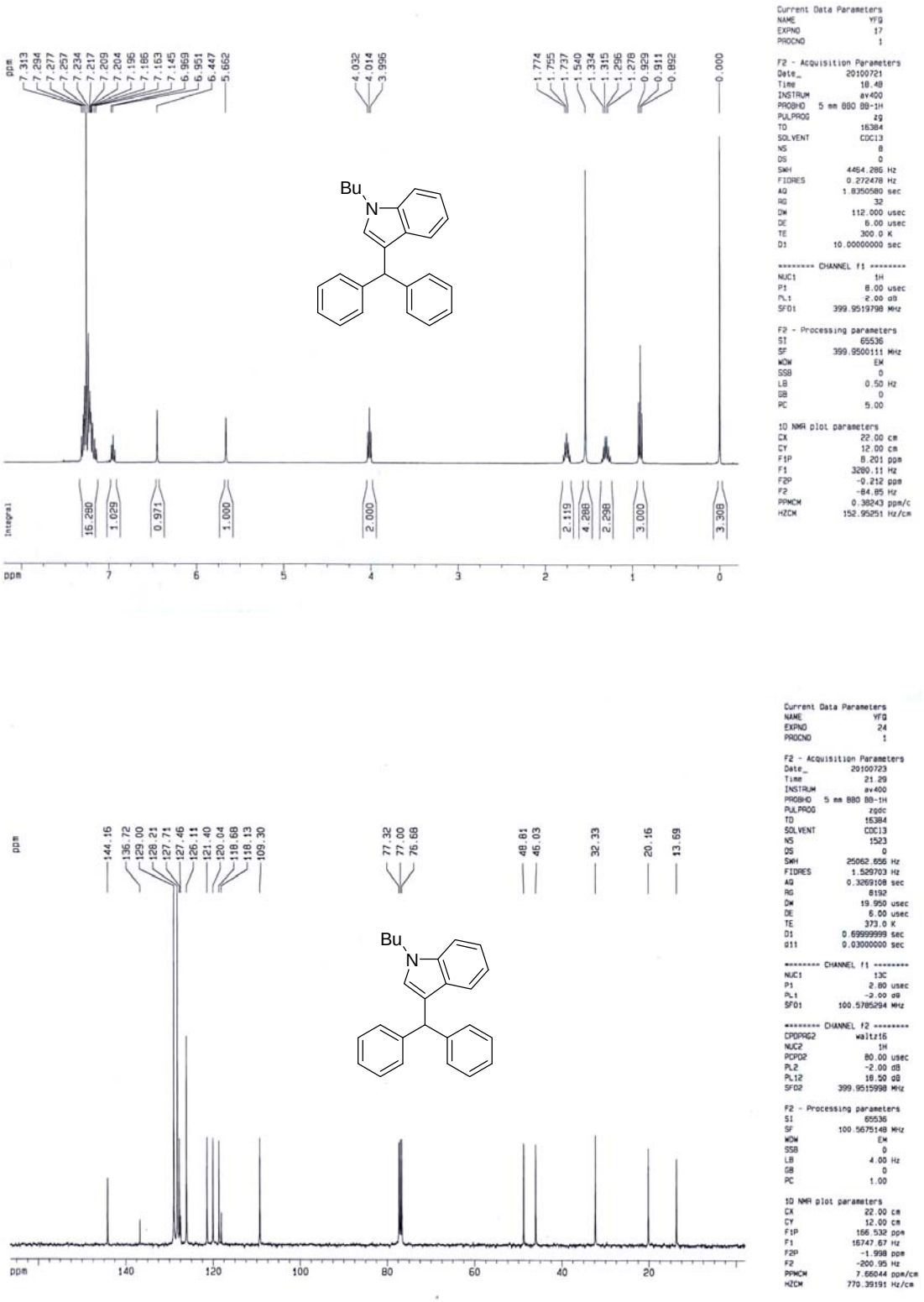

Figure S25. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **5f**

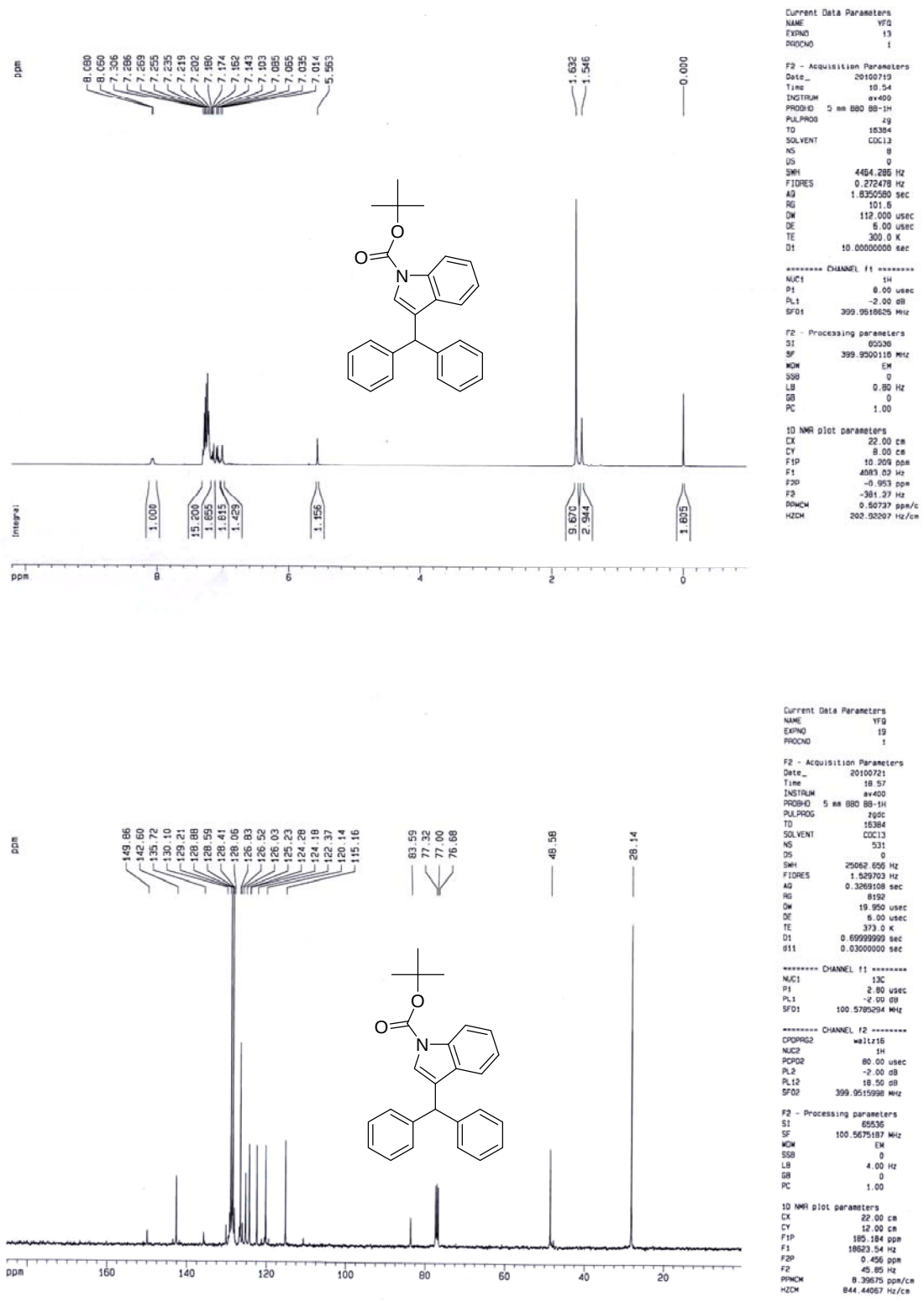

Figure S26. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **5g**

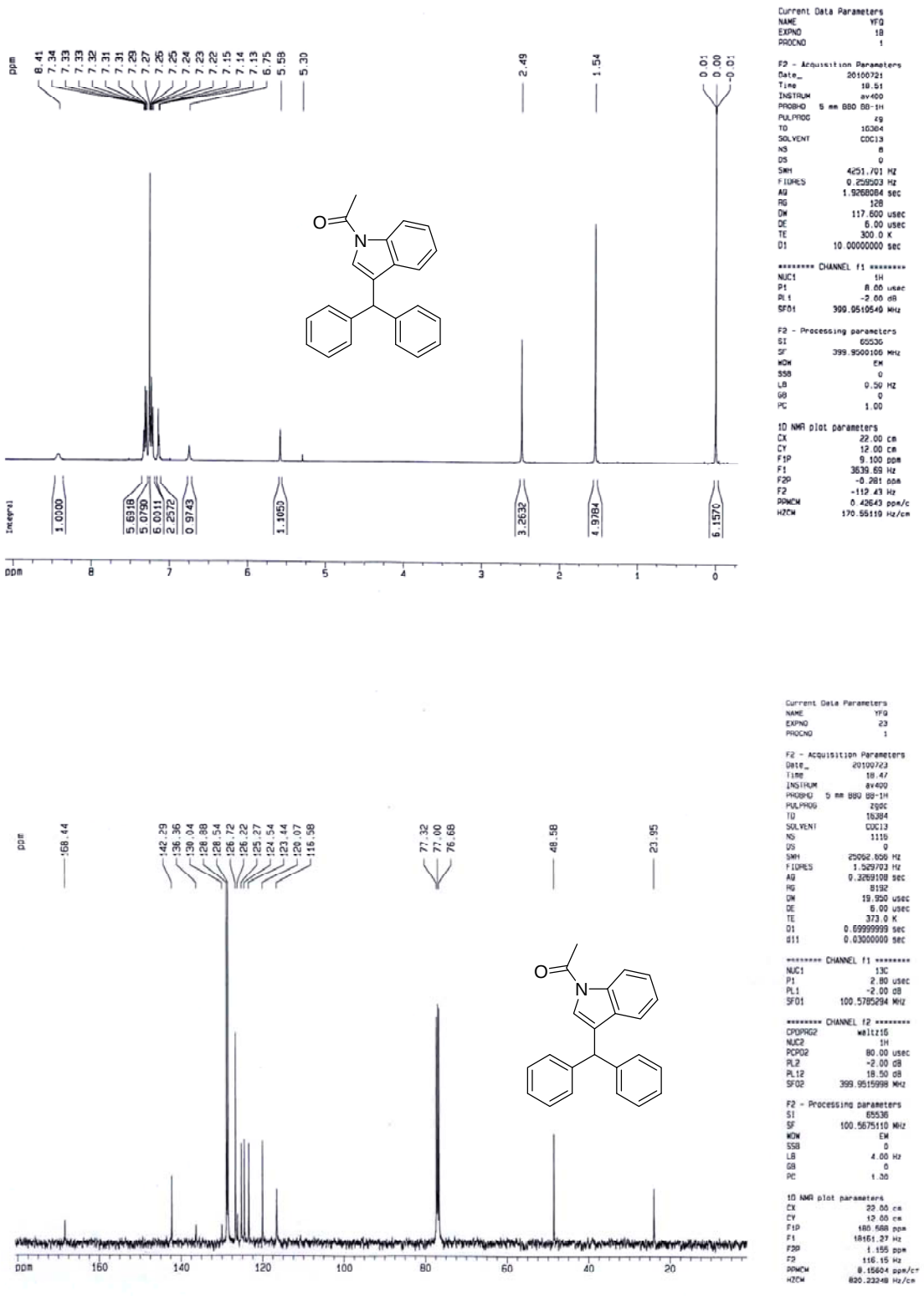

Figure S27. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **5h**

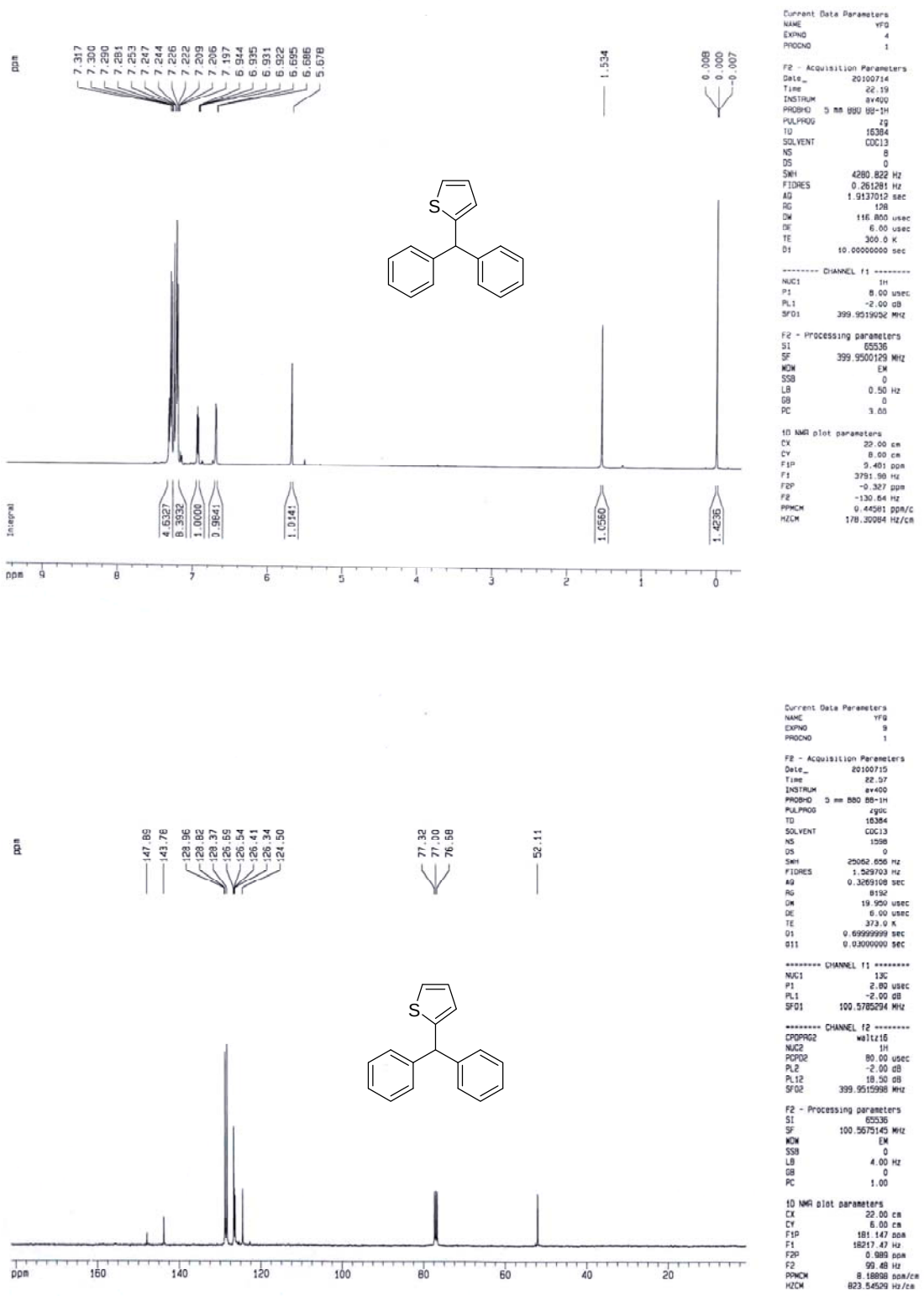

Figure S28. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **5i**

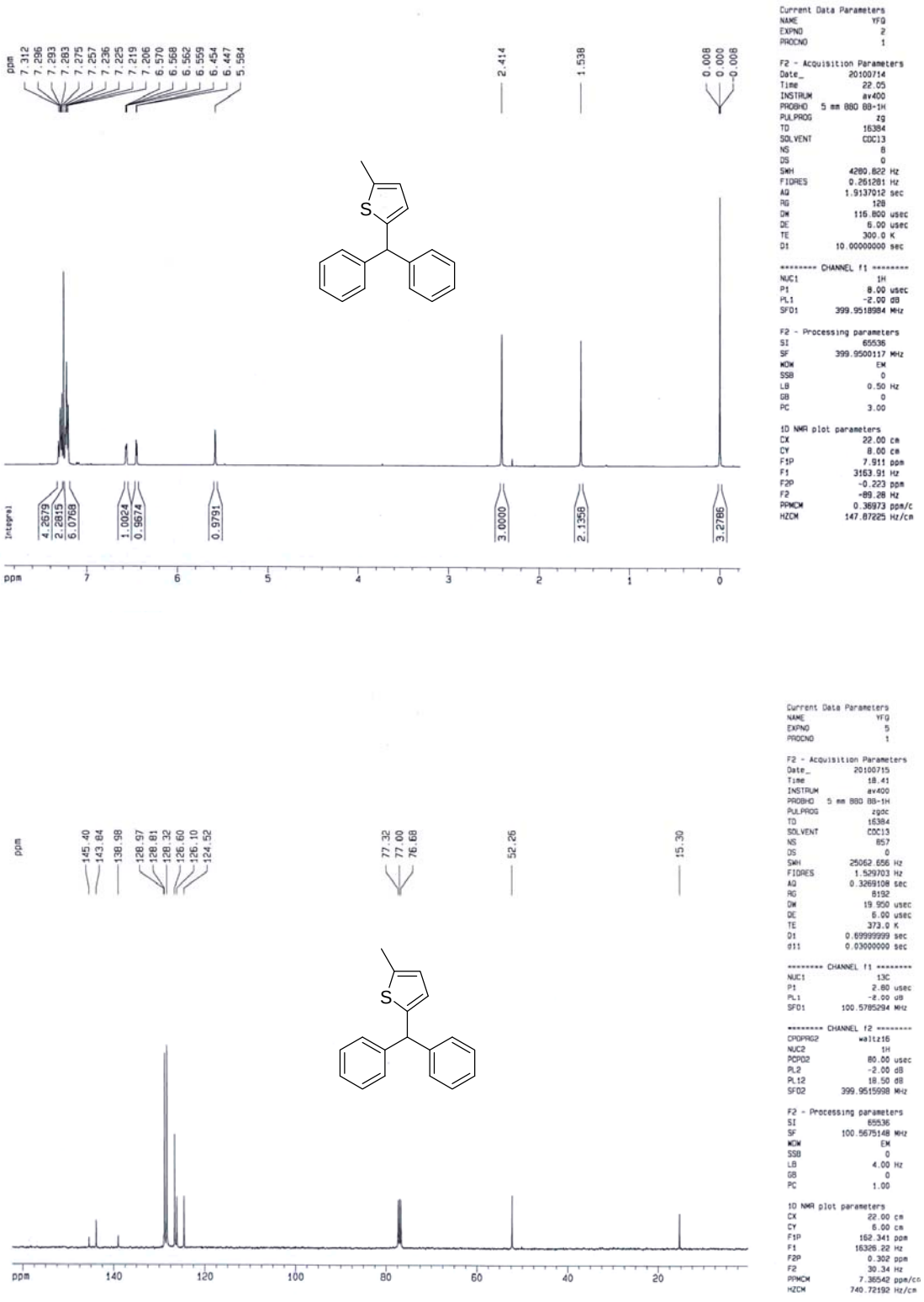

Figure S29. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **5j**

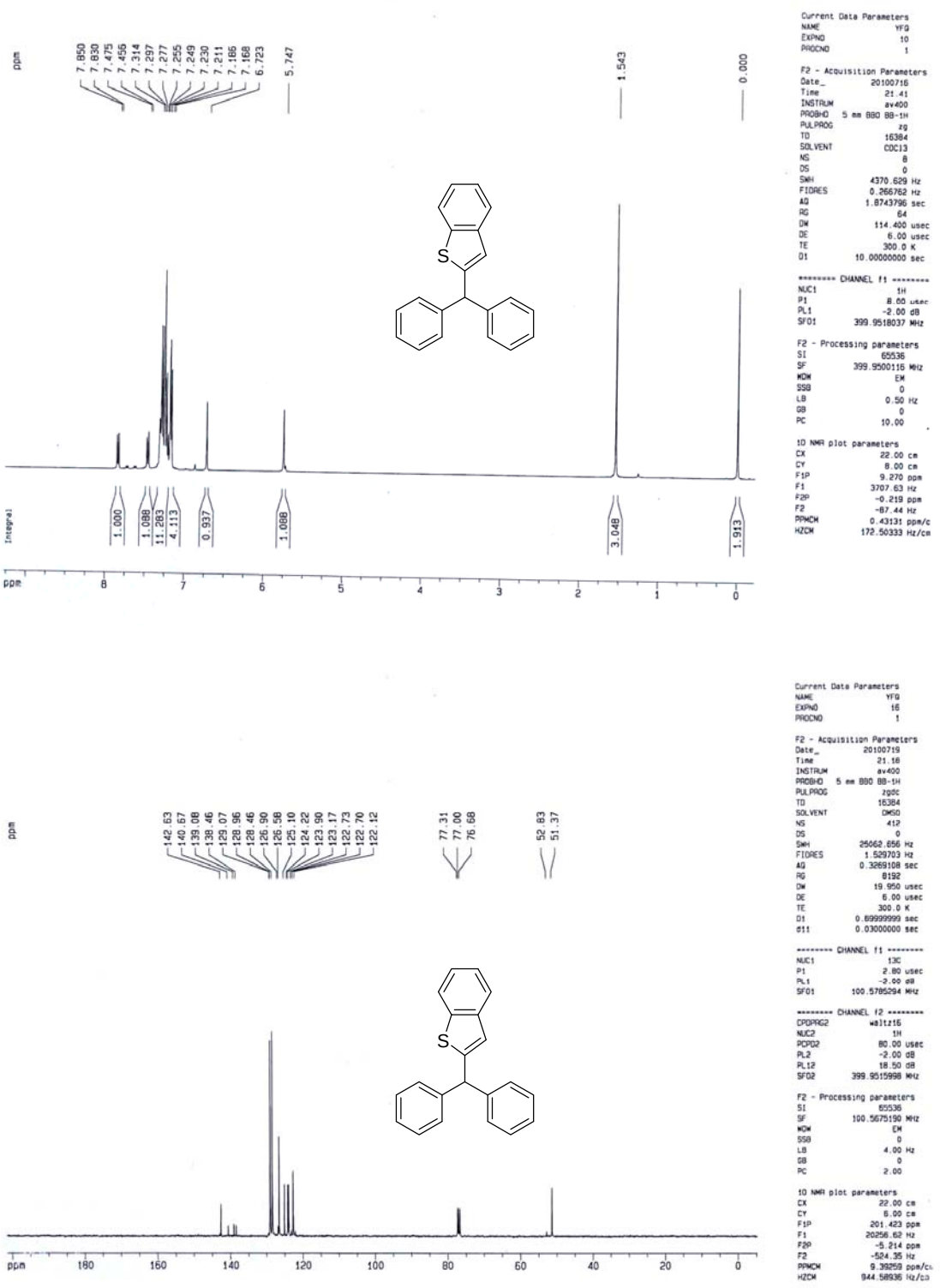

Figure S30. ^{1}H-(upper) and ^{13}C-NMR (bottom) spectra of compound **5k**